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**VAPOUR PHASE GROWTH OF THICK
MONOCRYSTALLINE GaN EPITAXIAL LAYERS BY
SANDWICH-METHOD**

Final Technical Report

by

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ABSTRACT The basic investigations leading to the fabrication of thick (more than 0.2 mm) monocrystalline layers of GaN on the silicon carbide substrates are performed. GaN layers were grown by sublimation sandwich-method in ammonia atmosphere. GaN polycrystalline powder and metallic Ga were used as a vapor source. The growth was carried out in quartz reactors both horizontal, and vertical types, in furnaces with high-frequency heating. The possibility of growing of thick monocrystalline GaN layers at growth temperature range from 1200 to 1230 ⁰ C without preliminary deposition of buffer layers with very high rates up to 1 mm/h is shown.				
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STATEMENT OF WORK

OBJECTIVES: To perform basic investigations leading to the fabrication of thick (more than 0.2 mm) monocrystalline layers of GaN

SCOPE: Outline of the scientific tasks:

- Choice of the substrate material available for GaN thick layers growth.
- Optimization of the substrate surface treatment before GaN layers deposition.
- Optimization of growth conditions of GaN thick layers with large substrate surface area (more than 1 cm²).
- X-ray control of the crystallographic quality, analysis of electrical, optical and paramagnetic properties of GaN materials and spatial distribution of structural defects in GaN.
- Deliver 10 samples GaN/ SiC, grown by sandwich method.

SUMMARY

The basic investigations leading to the fabrication of thick (more than 0.2 mm) monocrystalline layers of GaN on the silicon carbide substrates are performed. GaN layers were grown by sublimation sandwich-method in ammonia atmosphere. GaN polycrystalline powder and metallic Ga were used as a vapor source. The growth was carried out in quartz reactors both horizontal and vertical types in furnaces with high-frequency heating.

The analysis of the substrates for thick layers GaN growth with use of being available literary data are presented. Results of the analysis let us to choose a substrate from hexagonal SiC (α -SiC). Main advantages these substrates are their inertness to conditions of layers GaN growth, affinity presence both the lattice parameters ($\Delta a/a=3.4\%$) and thermal expansion coefficient (distinction in LEC=33%). We offer the ways of reduction of that discrepancy with using Al - doped substrates, previously radiated by high-energy particles.

The possibility of growing of thick monocrystalline GaN layers at growth temperature range from 1200 to 1230⁰C without preliminary deposition of buffer layers with very high rates up to 1 mm/h is shown.

Rocking curve measurements of the GaN layers grown by SSM reveal the full width of half maximum (FWHM) from 150 to 400 arc.sec. Three-dimensional 15-20 arc.sec. disoriented wurtzite domains looked like the hexagonal prism in size of cells of 50 nm were found. Correlation between the spectral luminescence characteristics, its spatial inhomogeneity and structural perfection of the grown layers was shown. Increasing of wide-band emission in visual spectrum and its spatial inhomogeneity was suggested to be caused by the local stoichiometry deviation. The Fe, Ni, Mn impurities states in the GaN crystals were discovered and identified by the EPR method.

The further improvement in crystal quality of GaN thick layers requires elimination of the following constructive lacks of the growing system, namely the ensuring stabilization of the operating modes of high-frequency heater and automation of temperature control in the growth cell. It is desirable to use the SiC substrates having previously deposited buffer layer of monocrystalline GaN .

List of Keywords:: gallium nitrides, thick epitaxial layers, substrate, silicon carbide, sublimation growth

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REPORT

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1. Introduction

1.1. Statement of the problem

Group III nitrides are known to be promising materials for solid-state electronics, including short-wavelength LED's and lasers, high temperature power and microwave devices [1,2]. The short wavelength lasers could increase current capability with data storage density over 1 Gb/cm^2 .

Early the main problems in GaN technology were held to be an inability to dope GaN p-type material and lack of lattice matched substrates that was responsible for high concentration of structural defects. Over last years much progress has occurred in obtaining of low resistivity p-type layers of GaN that make possible to begin large-scale production of highly efficient short wave LED's [2].

However up to now there were no lattice matched substrates available for epitaxial growth. The lattice mismatch substrates introduce strain and defects in GaN material and the only solution of the problem is to obtain GaN bulk crystals or thick epitaxial layers, which will be used as a substrate for fabrication of various epitaxial structures by known methods such as MBE or MOVPE.

The objective of this work is to perform basic investigations leading to the fabrication of thick (more than 0.2 mm) monocrystalline layers of GaN which may be used as substrates.

Outline of the scientific tasks is the next:

- Choice of the substrate material available for GaN thick layers growth.
- Optimization of the substrate surface treatment before GaN layers deposition.
- Optimization of growth conditions of GaN thick layers with large substrate surface area (more than 1 cm^2).
- X-ray control of the crystallographic quality, analysis of electrical, optical and paramagnetic properties of GaN materials and spatial distribution of structural defects in GaN.
- Deliver 10 samples GaN/ SiC, grown by sandwich method.

1.2. Background

Much progress has lately been made in the growth technology of group III nitrides, especially GaN. High quality GaN epilayers of hexagonal and cubic modifications are grown by MOCVD and MBE on sapphire and other substrates [1-5].

There are however some serious problems involved in the growth of high quality thick epilayers and bulk crystals of these materials, because a larger thickness normally leads to a lower structural quality [3]. As a result, the quality of such crystals does not meet the current requirements on semiconductor materials. Besides, there are difficulties in controlling the doping levels of both bulk crystals and epilayers. The behavior of intrinsic defects in GaN is still poorly understood.

We will first outline some specific features of these materials.

Nitrides (GaN, AlN) are assigned to compounds with relatively high chemical bond energy. This fact is the reason of very low velocities of relaxation processes in a solid phase. In result, effect of various surface factors on the crystal properties is very significant.

Growth of GaN from the own melt is extremely difficult due to high melting temperature (2800K) and very high dissociation pressure (>40 kbar).

The vapor phase of GaN is known to consist primarily of nitrogen molecules, so that equilibrium nitrogen pressure is very high, dozens and even hundreds of bars [6] at the growth temperatures. To avoid GaN decomposition, the growth should be performed in a high pressure chamber, which is difficult but possible to implement [7].

Another common way used in available growth systems is to supply of activated nitrogen vapors, say, ammonia, into the chamber [3]. But in this case, the growth goes on under nonequilibrium conditions, since ammonia is unstable at the growth temperatures. The temperature rise is accompanied by an increase in nitrogen partial pressure over the GaN surface. For this reason, the growth temperature is usually made lower but then it becomes hard to achieve high growth rates due to a low surface mobility of GaN adatoms.

It has been shown that GaN can crystallize in various modifications, or polytypes, which can co-exist in the same growth conditions [8]. Such GaN polytypes as wurtzite and zincblende are known to differ in the stacking sequence of double layers of group III and V atoms. The physical properties of GaN polytypes also show a variation.

It is clear from this description that GaN and other III-V group nitrides are technologically challenging materials. Really according to available data [3] fluctuations of temperature, growth rate, supersaturation, and vapor phase composition frequently result in sharp deterioration of crystal quality.

The next growth methods are used for growing thick GaN epilayers:

- Growth from solution in liquid Ga at high N₂ pressure [7];
- Hydride gas phase epitaxy;
- Sublimation growth.

10 mm GaN bulk crystals with surface area about 70 mm² were grown by S.Porowski et al. in the increased volume high pressure reactor (p=10-20 kbar) [7]. However this method is rather difficult and its prospects are not clear.

The method of hydride gas phase epitaxy [5,9], is more attractive. High quality thick GaN layers (up to 0.8 mm) were grown by this method using buffer layers ZnO or GaN. However, monocrystalline growth was possible only after preliminary deposition of buffer layer. Only polycrystalline layers of GaN grow on the substrate without buffer layer.

1.3. Features of sublimation sandwich method (SSM)

Earlier, we suggested an original method to control the epitaxial growth of high quality SiC [10, 11] and, later, GaN crystals [12] so called the sublimation sandwich method, which can be applied to other materials including decomposing compounds.

A simplified diagram of various sandwich growth cells is shown in Fig.1.1. The growth cell consists of a vapor source (1) and a single crystal substrate (2), on which a GaN crystal is grown. The source material is placed parallel to the seed crystal with a small gap. Ammonia can be introduced into the growth cell to prevent GaN decomposition. Growth conditions close to equilibrium can be created for a wide temperature range, from 1000 to 1300°C for

GaN. Such a system may be quasi-closed for its vapors, leading to congruent transfer of the sublimated material from the source to the seed.

The main advantages of this arrangement are:

- effective mass transfer of material from the source to the substrate at a maximum growth rate of about 1 mm/hour;

- the creation of nearly quasi-equilibrium conditions inside the sandwich cell providing a homogeneous deposition of sublimating substances in a wide range of temperatures, temperature gradients, and ambient pressures;

- controllable variation of the vapor composition in the growth cell in order to obtain a material with a desired doping level and impurity composition or with a deviation from stoichiometry;

- a smaller effective cell volume, which reduces the consumption of the sublimating material (the percentage of transported material is close to 100%), increasing its purity as to residual impurities;

- control over the nucleation and growth of a desired crystal polytype, e.g. of high quality heteroepitaxial layers of SiC polytypes: 4H, 6H, 3C, and 15R;

- effective growth in the absence of surface-active impurities usually serving as transporters of sublimating material;

- easy creation of uniform thermal fields inside the sandwich as a means of improving the crystal quality;

- control of the intrinsic point defect ensemble in the on-grown samples owing to the wide temperature range used (900° C for SiC and 300° C for GaN), inaccessible to other methods;

- easier access to fundamental data on the growth process, possible simulation of the mass transfer processes during sublimation, and the model verification; this provides a better understanding of the crystal formation and elementary doping processes.

GaN layers were first grown by sublimation sandwich method on silicon carbide and sapphire substrates in a horizontal quartz reactor with RF heating [12, 13].

We shall note, that this method became to use recently for GaN monocrystalline epilayers growth other groups in USA, Germany [14] and Japan [15].

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2. The Choice of Substrates for GaN Epilayer Growth

2.1 Influence of the Lattice Parameters

When choosing substrate material for growing single crystal epilayers, one should keep in mind the following factors:

- the crystal structure;
- the lattice parameters;
- the thermal expansion coefficient.

It is important to know the elastic properties of both the substrate and the crystal to be grown, as well as the ductile-brittle transition temperatures. No doubt, the best substrates for epilayer growth are those made from the same material; this condition is known as homoepitaxy. Indeed, high quality epilayers and devices on their base have been produced using GaN substrates [1]. However, it is still difficult to produce perfect substrates, because the grown GaN single crystals have a large size and low structural quality.

Because of the lack of perfect substrates, of great importance is the problem of finding a suitable material for epilayer growth. It has been shown that a greater lattice mismatch of the layer and the substrate considerably deteriorates the characteristics of devices made from such structures.

The stress in a GaN heteroepilayer is reduced during the growth and cooling by introducing misfit dislocations on the interface.

For example, Monemar [2] found an appreciable difference in the exciton behavior in GaN epilayers grown on different substrates, which might be due to stress gradients in the layers. The importance of the stress effect was demonstrated by an appreciable change in the valence band dispersion in the layer plane and, hence, in the hole and exciton masses.

To grow a certain GaN modification, substrates of a similar crystallographic structure are preferable. For example, cubic GaN layers can be grown on Si, GaAs, GaP and 3C-SiC substrates. Hexagonal GaN epilayers are, on the contrary, usually grown on sapphire, 6H-SiC and other substrates with the hexagonal structure. Much effort has so far been made to study wurtzite GaN because it is more stable than cubic GaN.

The characteristics of materials used as substrates can be found in Table 2.1.

Among other potential materials for substrates are spinel, NGO, TiO_2 , and LiAlO_2 [3].

Wurtzite GaN epilayers are usually grown on (0001) substrates, so we first focused on the lattice parameter mismatch along the a-axis ($\Delta a/a$). These data are presented in Table 2.2. There is a data spread concerning the lattice parameter mismatch for the GaN/ Al_2O_3 system. Evidently, the most probable values are $\Delta a/a = 14\text{--}16\%$ [4].

It is clear from Table 2.2. that ZnO, AlN, LiAlO_2 , and SiC have parameters similar to those of GaN. Nevertheless, GaN layers have so far been grown on sapphire substrates, because this material need not be pretreated or precleaned and is stable at high temperatures. But recently, the development of optimized buffer growth techniques has permitted one to minimize the effects of the lattice and thermal expansion mismatch to produce high quality MOVPE materials. GaN and AlN buffer layers, usually 300Å thick, are deposited at low temperature to produce a uniform coverage of amorphous material. Subsequent heating to the growth temperature of 1000°C transforms the buffer layer to a two-dimensional single crystal interface ready for epitaxial growth. Today, GaN layers grown by this method are the world record ones. There are however problems associated with residual stresses and defects producing a great lattice mismatch and differences in thermal expansion, the latter playing a major role in the post-growth cooling and annealing.

Good results have been obtained with sapphire substrates having a pre-deposited ZnO layer [5]. This approach has been shown to indicate the way for growing thick, high quality GaN layers.

Recently, interest in SiC substrates has considerably increased due to the progress in the growth of large bulk SiC crystals of 1–1.5 inch diameter and larger. Commercial production of such crystals has been started by the CREE company in the USA [6]. In this connection, we would like to emphasize that the sandwich method we have suggested allows the growth of not only thick epitaxial layers but also SiC bulk crystals (6H, 4H, and 15R) with a large diameter — up to 1 inch [7].

The lattice parameters have been shown to depend on the following major factors [8]:

- free electrons expanding the lattice in proportion with the strain potential of the conduction band minimum;
- the polytype structure;
- impurities and intrinsic defects (vacancies, antisites, interstitials), the difference in their ionic radii relative to the substitutional host ions (size effect), and stresses including those caused by the lattice mismatch of the substrate and the layer;
- linear defects (dislocations and clusters of point defects).

Free electrons change the lattice parameters as

$$(\Delta x / x)_{\text{electron}} = -Dn / (3B)n,$$

where x is the lattice constant, n is the electron concentration at the conduction band minimum, Dn is the strain potential of this minimum (-10eV for GaN), and B is the bulk modulus equal to 2×10^{11} Pa. This means that the free electron concentration of $1 \times 10^{19} \text{ cm}^{-3}$ for GaN should raise the lattice constant approximately by 0.01%.

The lattice parameters for the various SiC polytypes can be found in [9]. They indicate a higher lattice parameter c and a lower parameter a , as the proportion of hexagonal SiC becomes larger. The lattice parameter variation does not exceed 0.1% for various polytypes.

Later, we will discuss in more detail the effect of impurities and defects on the SiC lattice parameters with emphasis on those leading to their higher values, since the lattice constant of SiC is smaller than that of GaN.

One example of such an impurity is aluminum substituting silicon in the SiC lattice. The tetrahedral radius of an Al atom ($r_{Al}=1.26\text{\AA}$) is larger than that of Si ($r_{Si}=1.17\text{\AA}$). Besides, Al possesses a high solubility level in SiC ($C_{Al}=2\times 10^{21}\text{ cm}^{-3}$) [10], leading to a larger lattice constant, but this gain is only 0.01-0.02% in heavily Al-doped SiC crystals [11].

The formation of intrinsic nonequilibrium defects, say, during the crystal irradiation by high energy particles (ions, fast neutrons, electrons) also increases the lattice parameters, e.g. they increase by 1% after 10^{21} cm^{-2} neutron irradiation [12]. Nonequilibrium defects have been shown to be stable up to 1300–1400°C. This temperature is higher than the GaN epilayer growth temperature.

Nonequilibrium defects produced during the crystal irradiation or growth may form stable clusters, vacancies and interstitials, which affect the mechanical and other properties of the crystals. Irradiated SiC crystals with nonstoichiometric defects tend to cracking, which results in deterioration of their microstrength characteristics [13].

The lattice mismatch of the substrate-epilayer system is also affected by the substrate orientation. It is interesting that different mismatch values can be observed for the polar (0001) faces. This fact was interpreted in [14] as being due to the contribution of the interface charge from the ionic portion of the binding energy. Estimation of the lattice mismatch at the GaN-SiC interface has given the following values: 3.4% for both assumingly uncharged GaN/SiC interfaces, 2.6% for the charged (0001)-Si interface, and 5.6% for the charged C interface.

This assumption has been used to explain the essential difference in the surface structure of GaN layers grown on the (0001) C and (0001) Si sides of a SiC substrate [15]. Indeed, GaN layers grown on C-terminated (0001) SiC substrates exhibit a pyramidal structure, which may be accounted for by a considerable local micromismatch. On the other hand, GaN layers grown a Si surface are smooth because of a smaller mismatch on this surface. Therefore, the Si surface is preferable to the C surface for the growth of GaN layers on a (0001) SiC substrate.

2.2 Effect of the Thermal Expansion Coefficient

Thermal expansion of single wurtzite GaN crystals has been studied in the temperature range from 300 to 900 K or from 80 to 820 K. Maruska and Tietjen [16] reported a linear temperature variation of the lattice constant with the thermal expansion coefficient $+5.59\times 10^{-6}\text{ K}^{-1}$. The gain in the lattice constant c shows a superlinear temperature dependence. The average coefficient of thermal expansion along the c -axis is $+3.17\times 10^{-6}\text{ K}^{-1}$ at $T+700\text{--}900\text{ K}$.

Sheleg and Savastenko [17] reported the thermal expansion coefficient to be $+4.52+0.05\times 10^{-6}$ and $+5.25+0.05\times 10^{-6}$ at 600 K for the normal and parallel directions relative to the c -axis, respectively.

Thermal expansion in GaN has recently been studied in [19]. Two kinds of samples were used: bulk samples and GaN epilayers grown on sapphire substrates. The latter had a smaller lattice constant, by about 0.03%, in the direction parallel to the interface plane. This difference was due to a greater thermal expansion of sapphire relative to the GaN layer.

The thermal expansion coefficient is shown to depend on many parameters, such as defect content, free-charge concentration, and stress [5]. This is likely to account for the considerable dispersion of experimental GaN thermal expansion data presented in Figure 2.1.

The difference in the linear expansion coefficients of the substrate and the epilayer gives rise to structural defects near the interface during the cooling to room temperature. This is especially dangerous at relatively low temperatures when the crystal loses its plasticity. The stresses produce cracks in the substrate and epilayer. The temperature range for the ductile-brittle transition is found to be 800–1100°C for SiC [19]. The respective range for GaN is not known exactly. However, the thermal stress due to different expansion coefficients of GaN and sapphire has been shown to arise mainly at temperatures below 500–600 K [20]; above this threshold, the lattice mismatch is close to zero.

Our experience shows that the relative deformation ($\Delta L/L$) in 6H-SiC crystals larger than 10^{-3} at room temperature is critical and leads to the crystal damage. Assuming that the plasticity of GaN is not smaller than that of SiC, we consider this value as being critical. Therefore, the difference in the expansion coefficients of the substrate and the GaN epilayer should not lead to deformation in GaN crystals larger than 10^{-3} on cooling from 800°C to room temperature.

Some expansion coefficients for materials used in GaN heteroepitaxy are presented in Table 2.1. Their temperature dependence for GaN, SiC and sapphire is shown in Figure 1. These data can be used to calculate the expansion differences between GaN and the substrate materials, which vary from -25% for sapphire to +33% for silicon carbide. Note that this difference for LiAlO_2 is -21% [3].

Thus, the available data and our own estimations of the lattice parameters and expansion coefficients for GaN and various substrate materials over the temperature range from 300 to 800°C indicate that hexagonal silicon carbide is preferable as substrate material for GaN heteroepitaxy.

This conclusion has been supported by the results of a study [21] on the residual stress in GaN epilayers grown on sapphire and 6H SiC substrates. In both cases, a large difference in the stress relaxation was observed. GaN layers on SiC substrates are subject to tensile stress and experiences a nearly complete relaxation. On the contrary, there is an appreciable residual stress in GaN epilayers on sapphire, and the stress conditions also differ. This could be attributed to a different signs of lattice mismatches and thermal expansion coefficients of sapphire, SiC and GaN. and SiC that reduce the epilayer strain during the post-growth crystal cooling.

Moreover, SiC crystals may have any polarity and conductivity (both n- and p-type) with a wide range of resistance, from 10^{-2} to $10^{-8} \Omega\text{cm}$.

2.3. Conclusion

SiC substrates are preferable for heteroepitaxial growth of GaN layers of large area and thickness. Such substrates are well matched with the GaN layer in both the lattice parameter

and the thermal expansion coefficient. The GaN/SiC lattice mismatch can be reduced by using Al-doped 8H-SiC irradiated by high energy particles. Various manifestations of stress due to the lattice and expansion mismatch in SiC and GaN reduce the epilayer strain during the post-growth crystal cooling.

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3. Optimization of Substrate Surface Treatment before GaN Layer Deposition.

3.1 SiC Substrate Growth and Characterization

The substrates to be studied were SiC crystals, mostly 6H, differing in the growth conditions. Group-I substrates consisted of Lely crystals grown at a temperature close to 2550° C [1]. Such crystals grow as wafers with at least one well-defined habit (0001) face. This crystal shape facilitates the production of substrates with a singular surface having a very small misorientation angle. The crystals of this group possess a fairly high structural perfection, as is evidenced by X-ray analysis [2]. The dislocation density varies between 10^2 - 10^3 cm⁻², and the density of micropipes and pores is usually below 10^1 cm⁻². However, the area of a Lely crystal is relatively small, and the linear dimensions rarely exceed 1 cm. Besides, the shape of the crystals grown under identical conditions varies considerably, e.g. crystals are often stretched in one direction.

For this reason, much effort has been made to obtain SiC substrates by other methods, in particular, by sublimation growth consisting in the transport of SiC vapors from a hot polycrystalline source to a cooler single crystal substrate. Deposition at low pressures (< 0.1 atm) made it possible to reduce the growth temperature to 2100 - 2400° C. The first SiC crystals of 15 mm diameter were grown in this way by Tairov and Tsvetkov [3]. At present, bulk SiC crystals for substrate application are being produced in the USA, Germany, Japan, and Russia. The best commercial SiC ingots are made by the CREE firm (USA). For example, 6H -SiC and 4H -SiC ingots with a 2 inch diameter have been produced [4] for GaN epitaxial layer growth. The crystals are usually of n-type conductivity due to the presence of donor nitrogen, whose concentration varies within $(0.5 - 3) \cdot 10^{18}$ cm⁻³.

The growth techniques employed by various research groups do not differ much, though they bear different names. More often, the method of growing SiC bulk ingots is termed as a modified Lely technique.

Modified Lely SiC single crystals have been studied by several workers [2, 5], who have found that their structural perfection is still inferior to that of conventional Lely crystals. For example, they have much higher densities of dislocations (10^4 cm⁻²) and micropipes (10^2 cm⁻²) and often contain inclusions of other SiC polytypes. Also, there are misoriented and strained regions distributed nonuniformly over the wafer area. Such defects are readily detectable by X-ray diffractometry. They lead to much larger halfwidths of the reflection curves. SiC crystals of this kind were found to have a mosaic structure due to the co-existence of large and small structural units slightly misoriented relative to one another [5].

The presence of residual strains in SiC ingots, absent from Lely crystals, seem to be associated with the lower growth temperatures. Indeed, we have shown that relaxation of the strains introduced by mechanical damage of the crystal surface occurs at fairly high

temperatures and is not completed even at 2300° C [6]. Note also that the growth temperatures of bulk crystals are insufficient for the annealing of nonequilibrium point defects, which may persist as clusters or associates detectable by various physical methods [7].

In the present work, we have used SiC substrates grown by sublimation sandwich-method (SSM). As early as 1970, we first demonstrated the possibility to grow high quality SiC layers, using the SSM, by which we achieved high growth rates (> 1 mm/hour) at relatively low temperatures (about 1900° C) in vacuum ($P \sim 10^{-5}$ Torr) [8]. Later, we employed the same technique for growing 6H.15R-SiC and 4H-SiC ingots of 1 inch diameter [9]. From these, we made SiC substrates to be used in the present work (Group-II substrates).

The structural perfection of the Lely and sublimation SiC substrates was tested by X-ray diffraction. A standard (omega) scan was used for the characterization of SiC substrates and GaN epilayers. The crystal monochromator in the X-ray diffractometer was a (0001) SiC Lely crystal. The full width at the half minimum (FWHM) of the crystal was less than 13 arc.sec for the (0006) rocking curve and 8 arc.sec for (00012). The high precision of the X-ray optics adjustment provided standard rocking curves for the characterization.

The FWHM measurements of the SiC substrates grown by different techniques are summarized in Table 3.1. On the whole, they indicate a high quality of the substrates produced by sandwich sublimation: they have been found to possess the same structural perfection as crystals grown by the modified Lely technique. There were proposed normalized method of characterization based on usual x-ray rocking curves (RC) and small-angle scattering of x-ray (S-AS) method. Each measurement were joined to another. The broadening of RC and the shape of S-AS spectrum revealed treatment quality of the surface, domain size (50 to 500 Angstroms) and their misorientation from 5 to 15 arc.sec..

In the Fig. 3.1. we see three rocking curves: (0006), (000 12) from the random part of the crystal and (0006) from the best part of the Lely crystal. It is well seen that (0006) monochromator is in good agreement with (0006) rocking curve. In common thinks it is forbidden to compare (006) and (000 12) rocking curve. In the special choosing we find the place with narrow RC close to theoretical data.

In the Fig.3.2 we see (0006) RC for SSM substrate. The wide RC corresponds to the surface of the plate after saw. The narrow RC corresponds to polished and etched surface. It is seen that the quality of Lely crystals coincide with SSM substrates.

3.2 Substrate Preparation for GaN Layer Growth

The SiC crystals used as substrates represented wafers of 450 - 500 μm thick with the base surfaces close to the (0001) plane. The substrates had a misorientation angle varying between 0 and 5° with respect to the (0001) face. The samples were subjected to pre-grinding and polishing with diamond pastes followed by etching in the alkali KOH melt for several minutes. The (0001) C face is known to etch fast, at a rate 20 - 100 times that of the (0001) Si face. The Si face, unlike the C face, is characterized by selective etching occurring mostly in the vicinity of structural defects—dislocations, scratches, second-phase inclusions, etc. This fact can serve for identification of the surface type, because micropipes, dislocations, pores, scratches, and other mechanical defects become decorated on the Si face. The dislocation density in the substrates of interest varied from 10^2 to 10^4 cm^{-2} and the micropipe density was 10^1 cm^{-2} or less.

The structure of the grind-damaged near-surface layer of the crystal is, according to [10], complex and includes an inner sublayer with residual strains. The total thickness of the damaged layer is 30 - 50 μm ; it should be removed prior to the epilayer growth, because on heating above 1100° C the relaxation of residual strains occurs to form dislocations [11]. For this reason, we removed all the damaged layer before the growth.

With the (0001) C face, this was done by chemical etching in the KOH melt at 480° C for 30 min to remove a 50 μm layer. This procedure proved impossible for the polar (0001) Si surface because of its selective etching and a low etching rate (10^2 times less than for the (0001) C face). Ion-plasma etching is normally used in this case [12] but its rate is too low to remove all the damage defects from the subsurface layer.

To avoid these difficulties, we used a specially developed technique — sublimation etching [13] based on the same sublimation sandwich-method with the exception that the growth cell was placed in a thermal field with an opposite temperature gradient as compared to the growth gradient. In other words, the SiC wafer is at a higher temperature and evaporates during the heating. The sublimation etching rate varies not only with the temperature but also with the temperature gradient and the vapor composition [14]. In absence of impurities, the desired evaporation rates (about 1 $\mu\text{m}/\text{min}$) are attained at about 1800° C.

An important condition for quality etching is excessive Si vapor in the sublimation cell, since even a slight Si deficit results in partial graphitization of the surface to be evaporated, leading to its lower morphological quality. For this reason, the sublimation etching is carried out in a sandwich containing excessive silicon. A similar effect can be achieved by introducing tantalum [15] or some other impurities into the cell for gettering the excessive carbon.

To optimize the treatment of the SiC substrate surface used for the epitaxial growth of GaN layers, we studied the influence, on the layer quality, of structural and morphological substrate defects, of a pre-deposited buffer layer, and of the way of removing the damaged layer, i.e. polishing, chemical or sublimation etching. The growth occurs on the polar substrate surfaces, (0001) C and (0001) Si, and on those misoriented at an angle of 0.5 and 5° C to them. The substrate thickness varied from 150 to 450 μm in some experiments.

The on-grown layer quality was controlled by a complex analysis of the layer parameters by optical and scanning electron microscopy, X-ray diffraction, and the luminescence technique.

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4. Optimization of growth condition of GaN thick layers with large substrate surface area

4.1. GaN Epilayer Growth by Sublimation Sandwich- Method

GaN epilayers were grown in the quartz reactors. Laboratory scale lamp RF generator had power about 8 kW. We used reactors both horizontal and vertical types. Typical horizontal set-up for growth of GaN layers are presented in Fig.4.1. The growth cell consisted of a vapor source and a substrate separated by a narrow gap of 5 to 10 mm, placed into a temperature gradient zone. The source temperature was heated to a higher temperature than the substrate. The temperatures of substrate and source are measured using W-Re thermocouple.

The crystal growth was performed in the temperature range 1100 - 1300° C with the temperature gradient between the source and the substrate varying from 10° C to 50° C. Before the deposition of a GaN epilayer, the reactive zone was evacuated at 500°C. The growth was carried out in ammonia gas flow at atmospheric pressure, with the flow rate varying between 10 and 50 liters/hour.

Metallic Ga or GaN powder has been used as source [1]. GaN powder was sintered preliminary in the same reactor through evaporation Ga melt in ammonia gas flow.

In this work we optimized the next parameters of growth system: source and substrate temperatures, source to substrate temperature drop, rates of heating and cooling, clearance in the growth cell and direction and rate of ammonia gas flow.

The lacks of growth apparatus are the next:

- R F generator had not a system of stabilization of output parameters that made difficult optimization of growth conditions in the growth cell.
- The automatic control of regimes of growth temperatures and gas flows was absent.

- Vacuum in the growth system was too low (about 10^{-1} Torr). Therefore, effect of the oxygen on the growth process remained a mystery.
- Reactor had small diameter (about 50 mm) that limited of growth cell sizes.
- Possibility of buffer layers deposition by vacuum condensation was absent.

This factors accounted for relatively low reproducibility of results that increased drastically amounts of experiments for optimization of growth conditions. In result more than 300 runs was carried out.

Taking into account necessity of performance of great number experiences and very high cost of the large sizes SiC substrates (\$ 100-200 for 1 substrate) we would have to use widely for optimization of growth conditions substrates of the smaller sizes ($<0,8 \text{ cm}^2$ area) . These substrates were grown mainly by Lely method.

Then at the following stage we studied specific problems of growing of thick GaN epilayers on the large sizes substrates.

4.2. Growth Kinetics

Single crystal GaN layers were grown in the temperature range $1050 - 1230^\circ \text{C}$. Note that the optimal growth temperature for such layers ($1150 - 1200^\circ \text{C}$) is higher than in other growth techniques. This enabled the authors of work [5] to suggest another name—high temperature gas epitaxy—for their technique absolutely identical to sandwich sublimation. This temperature range provided the growth of homogeneous GaN layers, containing no second-phase inclusions, at very high rates (up to 1 mm/hour). Interestingly, under optimal growth conditions perfect GaN layers could be obtained without buffer pre-deposition.

Free Ga inclusions were observed only at temperatures above 1230°C ; they were localized in the vicinity of structural and morphological defects. The epilayers grown under these conditions usually had a high pore density. On the contrary, at temperatures below 1050°C the probability of microcrystalline growth failure followed by formation of individual GaN crystals with a planar or prismatic shape became much higher. Then microcrystalline growth proved possible only on substrates with a pre-deposited GaN layer at maximum temperature gradients between the source and the substrate.

Figure 4.2 shows the temperature variation of the growth rate. One can see that it rises with temperature (up to 1200°C), reaching a value of 1 mm/hour. We would like to note that these are record rates for epitaxial deposition of single crystal GaN layers and several times higher than for hybriide gas epitaxy [1]. High deposition rates have also been achieved by other investigators using sandwich sublimation for GaN layer growth [4].

Further temperature increase leads to a sharp drop of the GaN deposition rate induced by thermal dissociation of the growing layer. This conclusion is supported by the appearance of Ga droplets on the surface.

Figure 4.3. shows the growth rate variation as a function of the gap size in the sandwich cell. It is seen that the rate decreases with the larger cell size, and the highest rates are achievable with small gaps where the growth process however becomes irreversible. One should bear in mind that as the gap size changes, not only does the Ga supply efficiency rises but the ammonia flow through the growth cell changes too, affecting the GaN growth rate. Obviously, the growth rate variation with ammonia flow has a complicated, nonmonotonic character. For example, the deposition rate of GaN decreases with low ammonia flows

because of its dissociation. But the growth rate decreases even in large ammonia flows due to the removal of Ga molecules from the sandwich cell.

4.3. Structural and Morphological Defects in GaN Epilayers

The epilayers produced have been found to contain the following types of defects: cracks, second-phase inclusions, pores, dislocations, and surface undulations. We will discuss them individually.

Cracks

Cracks appeared in epilayers of 20 μm thick and more and were localized primarily near the substrate-epilayer boundary. It is interesting that the luminescence in the vicinity of cracks changed from short-wave (dark blue and violet) to yellow. The probability of crack formation abruptly decreased with decreasing rate of the substrate cooling. It seems clear, therefore, that their formation is associated with the differences in the thermal expansion coefficients.

We have also found the dependence of the crack density on the substrate thickness and misorientation angle relative to the (0001) face. The appropriate technological corrections have been introduced to minimize the probability of crack formation in GaN epilayers grown on SiC substrates.

Second-phase inclusions

Usually, second-phase inclusions represent free gallium and are observed in the vicinity of pores and other morphological defects. The inclusions are due to the active nitrogen deficiency near the growing surface, so a more powerful ammonia flow into the growth cell and a lower growth temperature contribute to the elimination of such defects.

Voids and micropipes

These are the most characteristic defects in thick GaN epilayers. Their density strongly depends on the growth conditions and the state of the substrate surface. The voids density usually rises with increasing growth temperature, decreasing source to substrate temperature drop or with decreasing ammonia flow. We suggest that porosity is associated with local GaN dissociation and formation of free gallium because of the deficit of active Ga. The voids formation is stimulated also by a poor substrate surface treatment, e.g. incomplete removal of material after the damaged layer grinding, or the presence of the morphological defects on the substrate surface. Elevated voids density has also been observed in GaN epilayers deposited on substrate surfaces with a 1- 5° misorientation relative to the (0001) face. What causes this effect is not quite clear yet.

Note that voids and micropipes present in the SiC substrate are inherited by the GaN epilayer, so the best epilayer samples were obtained on SiC substrates of high structural perfection.

Morphological defects

The morphology of GaN epilayer surfaces strongly depends on the substrate orientation. Relatively smooth layers grow on the (0001) Si face. Under the same conditions, GaN epilayers grown on (0001) C substrates have a rough surface covered by hexagonal growth undulations. At higher growth rates, individual prismatic crystals arise on the C face. We attribute the above defects to the fact that the growth process occurring on the carbon face involves three-dimensional seeds, while on the silicon face two-dimensional GaN seed are formed and then outgrow tangentially. We discussed this difference in the epitaxial growth

mechanisms earlier [5] and interpreted it as being due to the specific chemical bonding of silicon and carbon atoms resulting in a higher surface energy of the (0001) Si face as compared to the (0001) C face.

Use large size substrates creates additional problems. The principal of them are the following:

- Strains in the epilayer (and substrate also) increase. In case of thick GaN epilayers (more than 0.15-0.2 mm) chances that both substrate and epilayers may be cracks are good. Besides, epilayer may break away from substrate.
- The provision of conditions for homogeneous GaN epilayers deposition become more difficult due to dissociation of ammonia gas. This causes the appearance of individual column-type polycrystals and free Ga inclusions on some parts of the substrate. Epilayers are usually irregular in thickness.

To solve these problems we modernized our growth cell and system of ammonia gas supply. Our investigations have shown, that vertical-type reactors are more preferable for successful growth of GaN epilayers on the large size substrates.

4.4. Discussion

Now we discuss next problems of GaN sublimation growth on the SiC substrates depending on growth parameters conditions:

a. Conditions for monocrystalline growth:

The major contributory factors for monocrystalline growth on the SiC substrate (without buffer GaN layer) are temperature of a substrate; source to substrate temperature drop; type of substrate surface; the partial pressure of active nitrogen (ammonia) near the substrate and source surface.

- The first stage of epilayer growth (nucleation) is to be proceeded at rather high temperatures. However in this case high partial pressure of active nitrogen is required that are difficult to realize. Therefore the optimal temperature range of high rate growth is usually rather narrow (about 30-50 °C). This range is diminished yet with increasing of the substrate sizes.

- The monocrystalline growth of GaN is possible in a rather narrow range of source to substrate temperature drop (ΔT). At low ΔT there are non-continuous overgrowing of the substrate surface. At high ΔT polycrystalline growth of GaN takes place.

The best epilayers were grown on the vicinal (0001)Si substrate surfaces having small misorientation ($<30^\circ$). It was very difficult to obtain monocrystalline layer on highly off-axis substrates. The improvement of growth quality may be reached by special preliminary heat treatment of substrate in vacuum and in presence of Al and N vapors. Nevertheless, it is desirable to use the SiC substrate with preliminary deposited GaN buffer epilayer. Monocrystalline AlN buffer layer are suited obviously for GaN epilayers growth. Such layers may be deposited on the SiC substrate by sublimation sandwich method.

b. Cracking of substrate/epilayer structure; breaking away of epilayers from substrate.

This problem are due to differences of thermal expansion coefficients of SiC substrate and GaN epilayer which responsible for strains both in the substrate and epilayer. We found that maximal strains in the SiC/GaN structures are generated during crystal cooling in the temperature range from 600°C to 200°C. We try to diminish rate of cooling in this temperature range using special additional heaters. In result the duration of cooling was changed from 10 min to 3 hours. Use thin substrates (about 0.18 mm) also allow to diminish probability of cracking.

c. Voids and second phase inclusions

The following growth conditions cause the arising of voids and second phase inclusions:

- Low supersaturations or small source to substrate drops;
- Ammonia -deficient atmosphere;
- Small clearance between source and substrate, when Ga microdrops may transfer from source;
- Contamination of substrate surface.

4.5 Conclusion

The present study has demonstrated the possibility of growing single crystal GaN epilayers on SiC substrates at high rates, up to 1 mm/hour. The substrate quality has been found to affect significantly the epilayer perfection. The best GaN epilayers were grown on (0001) Si substrates with small misorientation angles by using sublimation etching. The growth of quality GaN epilayers on buffer-free substrates at temperatures of 1150 - 1200° C has been shown.

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5. Analysis of electrical, optical and paramagnetic properties and spatial distribution of structural defects in GaN epilayers

5.1. X-ray characterization of structures quality

5.1.1. X-ray diffractometry

In our experiments we use standard (ω) - scan for characterization SiC substrates and GaN epilayers quality. In preparing X-ray installation (diffractometer URS-1.0 Burevestnik, Saint-Petersburg) we changed standard crystal keeper in the monochromator device. We changed base distances from monochromator to crystal in study too. We choose Lely crystal SiC (0001) as crystal-monochromator. The full width at half maximum (FWHM) for this crystal is less than 13 arc.sec at (0006) rocking curve and 8 arc.sec at (000 12). High - accuracy adjustment of X-ray optics let us to get standard rocking curves for our characterization. using $\text{CuK}\alpha_1$ radiation in combination with a plane SiC (0001) monochromator crystal

The structural quality of GaN layers was studied by X-ray diffractometry (XRD) and Soller slits for the determination of peak width with high resolution. The angular resolution is approximately 3.6 arc.sec. which is smaller then the diffraction width of the peak observed from GaN.

The experiment utilized a 4-circle diffractometer which allowed the access to a large volume of reciprocal space. Several different types of scans were used to characterize the layers. Thus, if the film has the (0001) orientation, Θ - 2Θ diffraction scans of these peak can determine the difference between the two polymorphs. The periodicities of the two structures are fundamentally different: $a=3.186\text{\AA}$, $c=5.176\text{\AA}$ for wurtzite structure and $a=4.530\text{\AA}$, ($2d_{220}=3.210\text{\AA}$, $2d_{111}=5.231\text{\AA}$ - for zinc-blende in wurtzite set.

We have found only the wurtzite phase and could not detect the zinc-blende GaN phase which often coexists in experiments of other authors. The presence of a coherent crystalline component in all of the grown layers was confirmed by well - defined, essentially Lorentzian x-ray diffractometer peaks (Figs 5.1.1; 5.1.2).

Double crystal X-ray diffraction (0002, $1\ 1\ \bar{2}\ 4$) reflection profiles were recorded in parallel (**m-n**) setting with $\text{CuK}\alpha_1$ radiation.

In our experiments we studied more then 20 GaN/SiC structures. Some typical rocking curves are presented in Fig. 5.1.2; 5.1.3. For the most part the FWHM varied between 150 and 400 arc.sec. Rocking curve from one of the best samples is shown in Fig. 1.2. Curves are the profile of a heterostructure of 70 μm GaN stacked 300 μm SiC substrate illustrating the homogeneity present in epitaxial layers of this thickness. The layer reproduced the (0001) orientation (curve **a**) and its ($1\ 1\ \bar{2}\ 4$) direction (curve **b**) coincide with the ($1\ 1\ \bar{2}\ 1$) direction of the substrate. A sharp peak (0002) is resolved at $\omega=17.3$ arc.deg. corresponding to the known equilibrium GaN lattice constant (2.589 \AA). Other diffraction peaks of GaN polycrystalline structure were not observed. The intensities of SiC peaks are lower in comparison with GaN because of the adsorption in the GaN layer.

We have also performed measurements to examine the orientation of the grown layers. Rocking curves of ω , around the on-axis Bragg peaks were used to examine the orientation spread of the layer parallel to the surface normal (ω -scan). The spreading of in-plane orientations as well as the epitaxial relationship between substrate and layer axes in the plane were determined with ϕ -scans, in which the sample was rotated about its normal while ψ , 2θ and ω were held fixed at the peak position.

The Fig.5.1.2. illustrates well the difference between the crystallographic quality of the bulk substrate SiC and the epitaxial GaN layer. Rocking curve measurements of the GaN layers reveal the full width of half maximum (FWHM) of 150 arc.sec. The FWHM for SiC substrate is 130 arc.sec. The broadening of the rocking curve for the layers is caused by mosaicity, strains and destruction of the x-ray wave coherence by extended defects (like dislocations). The obtained FWHM value is compared with the best FWHM of 100 arc.sec. reported by Nakamura [1] and Ferita [2] ($\Delta\omega=40-100$ arc.sec. for GaN layers thinner than 1 μm) grown by MOCVD. Nevertheless, the present data represent a significant improvement over the previous 1 μm layer reported by MBE [3].

5.1.2. Small-angle scattering characterization of GaN/SiC interface.

Structural characterization of gallium nitride properties, studying surfaces and interfaces were carried out by routine X-ray diffractometry (XRD) and by the modified method of Small-Angle Scattering of X-rays (S-AS). (S-AS) will be convenient if objective is the study of crystalline diffraction patterns of 50-200 nm.

We used for our X-rays measurements thick films (0.2-0.3mm) of the GaN deposited on (0001) plane of SiC substrate and thin (0.003-0.005mm) films GaN deposited on sapphire ($\alpha\text{-Al}_2\text{O}_3$). X-ray rocking curves point out the difference in full width at half maximum (FWHM) of those structures. S-AS indicate difference in picture for those samples too.

We compare the shape data of ordinary X-ray diffractometry rocking curves of crystals with S-AS data. We propose the model of the domain wall grids for GaN deposited on SiC and Al_2O_3 .

GaN films deposited on the SiC had the three-dimensional 15-20 arc.sec disoriented domains. GaN domains distribute in liquid cluster model. It is seen by presence of strong incident peak and weak size-of-cluster peak. Fig. 5.1.4. Upper view of the grid of GaN domains looked like the network of 120 or 60 degrees 50 nm cell.

Estimation the length (perpendicularly surface) of those rhombical-hexagonal prisms (columns) was 200-300nm. In other words it is column model of GaN crystal growth discussed in papers devoted to electron microscopy studying this process.

We determine the interface character GaN/SiC as the texture of the second order. We claim that the stresses in the film realize as domain walls.

The transmission mode S-AS carried out on GaN deposited on sapphire registers that variations of density are distributed by the gas-like model Figs.5.1.5; 5.1.6. It coincide with referring transmission electron microscopy (TEM) data. [4,5]. The FWHM of X-ray rocking curves corresponding (000L) GaN reflection reveal a good quality GaN single crystalline film. As those films are 100 time thinner than SiC deposited, stresses can not crack across the film. We are to suppose that if the film would be thicker, the impurities can disorganize (cracks, domain walls formation) the film. The FWHM of such films are wider when film is thicker.

We can connect these phenomena with less organizing role of interface GaN/Al₂O₃. It has no such regular nature as GaN/SiC interface.

Searching the nature of interfaces let us to state the fact that GaN/SiC has very weak single crystalline rocking curve between GaN and SiC peaks. In GaN/ Al₂O₃ case signal level was low than noise level. It demonstrates that GaN/SiC interface has crystalline nature of intermediate GaN and SiC parameter. Similar picture corresponds to searching intermediate film of AlN in Ref.[7].

Structural characterization of GaN films grown under different growth conditions has also been carried out by number of workers. The major defects that have been reported in these films are dislocations, double positioning boundaries (DPBs), and inversion domain boundaries (IDBs). [7]

A typical low magnification image of a thick GaN epilayer grown on (0001) SiC, as viewed along an projection of the substrate has traces of interdomain boundaries. The GaN layer is epitaxial with respect to the substrate, also with an [0001] surface normal, and has the wurtzite crystal structure. Transmission electron micrograph showing the GaN film extended defect structure (Fig.2. from [4]).

It was observed that the wurtzite GaN was oriented epitaxially with the SiC substrate, i.e. the stacking direction of both crystals was parallel, and the domains were bounded by stacking faults. Such faults are commonly observed for materials which crystallize in more than one polytype. It appears that the partial dislocations associated with the stacking faults relieve the strain arising from the large lattice mismatch between GaN and the substrate, and allow the nucleation of the more stable wurtzite GaN domains, which have lower bulk energy, rather than the metastable zincblende material.

There was found domain structure of GaN. In the first time we could to estimate average size of those domains. [6] If electron microscope data get local view of cross-section of such film, composite X-ray researches (XRD and S-AS) get average integral picture of the inner situation inside the film. With the accuracy of less 0.1% we can find GaN zincblende phase. Naturally, the volume of boundary planes vanish to zero, and we can not notice it.

5.1.3. Discussion.

Plain view of zincblende and wurtzite phase differs in crystal plane packing. In other words stacking fault is equivalence of thin monolayer intermediate zincblende phase between wurtzite domains. We can not to see it in direct way. We can not claim that it is zincblende phase as whole, only the possibility of the such construction is proposed basing on our X-ray and the electron microscope literature references. [5] We can to estimate shape and volume of average column - like domain. In TEM case they can estimate a random column shape of random cross section.

The GaN film contains a high density, of planar defects primarily originating at the substrate-epilayer interface. These defects are mostly stacking faults and microtwins that lie along the equivalent planes. However, the defect density decreases with increasing distance away from the interface. [7] Twins are often observed to terminate within the epilayer as a result of intersection with a second twin or by a process of mutual termination at a twin/matrix interface, as observed previously in heteroepitaxial growth of epilayers(Fig.3(a) from [7]).

Closer inspection of the interface reveals that it is uneven, and a high density of dislocations is also evident in the GaN epilayer, especially close to the interface. These defects could represent a mechanism for strain relief close to the substrate surface. The nucleation of stacking faults and microtwins originating at the interface. The lattice misfit between SiC and GaN is 3.4%, 8.4% in *a* and *c* direction respectively and, as a direct consequence of such mismatch, continuity of lattice planes across the interface could be expected.

In SiC materials, the (0001) surface is close-packed, having the lowest surface energy of the principal surfaces. Stacking faults and microtwins on the (0001) planes are common growth defects and could provide an other mechanism for accommodation of the lattice mismatch at the substrate surface.

A low magnification image of wurtzite GaN deposited directly on (0001) 6H SiC as a substrate the epilayer can be characterized in terms of columnar grain growth and extensive stacking defects running parallel to the film/substrate interface. Close to the interface, the stacking sequence could be characterized as ..ABABAB.. corresponding to the hexagonal wurtzite stacking, but further away from the interface the stacking became almost random. The stacking faults are also evident from the streaking perpendicular to (0002).

In further efforts to obtain higher quality wurtzite GaN buffer layers were initially deposited on the (0001) 6H SiC substrate. The subsequent GaN deposited layer was effectively free of (0002) stacking defects and the stacking sequence was ..ABABAB.. across the entire width of the film.

Columnar grains in the GaN layer, due here to slight differences in growth conditions, project into the GaN film thus lending a polycrystalline nature to the latter but without any amorphous regions. The GaN buffer layer is obviously heavily faulted with many planar defects, whereas the GaN epilayer has comparatively few defects as compared with the buffer (See Fig.3(a) [4]).

This phenomenon coincide with our data of random gas-like distribution GaN domains grown on Al₂O₃ substrate and liquid cluster model of GaN domains deposited on SiC. In our earlier studies of GaN/SiC, [6] it had been found that the defect density in GaN layers was reduced for thicknesses in excess of 100 nm.

5.1.4. Conclusion

Rocking curve measurements of the GaN layers grown by SSM reveal the full width of half maximum (FWHM) from 150 to 400 arc.sec. The obtained FWHM values are compared with the FWHM of epitaxial layers grown by other known methods. Three-dimensional 15-20 arc.sec. disoriented wurtzite domains looked like the hexagonal prism of 200-300 nm length and the cells size of 50 nm were identified near the interface of SiC /GaN structure by the modified method of Small-Angle Scattering of X-rays (S-AS). Searching the nature of interfaces let us to state the fact that interface has crystalline nature of intermediate between GaN and SiC parameters.

Only wurtzite domains were observed in the GaN samples investigated. Here, the formation energies of wurtzite and zincblende phases of GaN are assumed to be roughly equal. Hence, lowering the energy of the heteroepitaxial system by nucleating defects, does not create favorable conditions for nucleating the wurtzite phase, which is thermodynamically more

stable. Nevertheless, because of large thermal (25% and 49%) and lattice (3.4% and 8.4%) mismatches[8], SiC is still not the ideal substrate material for wurtzite GaN heteroepitaxy.

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5.2 Electrical and optical properties and spatial distribution of structural defects

5.2.1. Introduction

The luminescence analysis is shown to be a powerful tool for control of crystal quality of the grown GaN epilayers. Sharp, narrow peak, at 3.47 eV corresponding to bound exciton recombination [1] is observed in high quality initial undoped GaN layers[2,3]. It can be assumed the degradation of crystallographic epilayer performance leads to the widening of above peak and wide-band emission appearance into view interval of the CL-spectrum caused by the deep emission centers.

This additional emission is considered to be to a donor-acceptor pair recombination which may originate from the deep levels caused by impurities and native defects which are introduced in the epilayer. It is known[1], par example, that acceptor impurities as Mg, Zn and Cd cause the bands appearance in visual interval of wave lengths dominantly in blue and violet parts of CL spectrum. Intensive yellow luminescence is very frequently observed in GaN-epilayers and some attempts were made to attribute this emission to the deep centers of unknown nature[4]. Earlier this emission was assigned to carbon [1].

Currently some serious evidence has been advanced that the center of yellow luminescence is an association including nitrogen vacancy [5,6]. The capability of several recombination mechanisms with participation of intrinsic defects and impurity is due to the dependence of GaN-epilayer luminescence vs the growth temperature, III/V molar ratio

[3,7,8] and substrate orientation [9]. The band-edge luminescence peak intensity of the GaN epilayer, grown on the oriented exactly (0001) plane is below considerably, than epilayer grown on misoriented plane [9]. Authors believe that slight misorientation decreases the interioration of deep impurities (Si, O and C, for example) and /or reduces the density of nitrogen vacancy.

The modification of the luminescence spectra is resulted from residual strain fields caused by the growth conditions [3]. This idea is confirmed by data published by Weeks et al [10], which demonstrates that there is tendency to shift of the luminescence spectrum to lower energies with decreasing GaN epilayer thickness. The assumption that value of residual strains is maximum near substrate-epilayer junction is valid. Really homoepitaxial layers of GaN have strong sharp exciton line and weak yellow band[11]. But these predictions require of further experimental confirmation.

Unfortunately, it is difficult to find an information in articles relative to the space luminescence inhomogeneity of grown layer. There is no question the luminescence inhomogeneities over the surface as well as epilayer thickness can essential to distort taken results. Obviously degradation of structure and morphologic epilayer performance leads to irregular luminescence. This conclusion is confirmed by followed experimental data. It was shown by Haramatu et al.[12] that inhomogeneous luminescence is measured when the surface growth process is carried out in a stepwise manner on vicinal plane. Next authors [13] also demonstrated that the microstructural defects (aggregates of dislocations) cause the CL inhomogeneity in the epitaxial GaN grown by MOCVD due to non-radiative recombination.

Currently the inhomogeneity luminescence of the GaN epilayers grown by sublimation sandwich method on the SiC and sapphire substrates have been studied. It was shown that structural and morphological defects cause the CL- spectral inhomogeneity of GaN-epilayers.

5.2.2. Experimental

The initial undoped GaN epilayer were grown by sublimation sandwich method on silicon carbide substrates in a horizontal quartz reactor with h.f. heating. The growth cell consists of a vapor source and a 6H- SiC single crystal substrate. The SiC substrates were oriented in the [0001]Si direction. The source material (Ga metal or GaN powder) is placed parallel to the substrate crystal with a small gap. The substrates of 6H SiC wafers grown by Lely method or sublimation sandwich method very used. High purity ammonia can be introduced into the growth cell to prevent GaN decomposition. Growth conditions close to equilibrium can be created for a wide temperature range, from 1000 to 1300°C for GaN. Such a system may be quasi-closed for its vapors adding to congruent transfer of the sublimated material from the source to the seed. As a result, we can grow bulk crystals and thick epilayers(about 0.1-0.5 mm thickness) at a rate of 0.2 to 1 mm/h. The effective volume of the growth cell can be considerably reduced to obtain low levels of residual impurities and a high probability of utilizing all evaporated material, when its transport in the cell is close to 100%..

The GaN epitaxial layers were characterized by photoluminescence in the spectral range from 3.5 to 0.5 eV using a high-resolution grating monochromator or a Fourier transform spectrometer. The samples were excited with the 325 nm line of a HeCd laser. In the detector system a photomultiplier or liquid -nitrogen cooled Ge or InGaAs diode was used.

Reflection and absorption measurements in the mid- and near-infrared at room temperature and 2 K were also performed on the Fourier transform spectrometer.

The color cathodoluminescence (CL) scanning electron microscopy (CCL-SEM) technique [14] was used for the study of the GaN epilayers deposited on the sapphire and silicon carbide substrates. The microscope was equipped with light detectors and a new backscattered electron detector. This technique using mixed true color contrast and black and white contrast recognizes local luminescence properties of materials, defects, specific inhomogeneities, and morphological peculiarities. Such capabilities allow to discovery of new information concerning growth structure of epitaxial GaN layers.

5.2.3. Results and discussion

We studied 25 GaN specimens grown by the above technique. The GaN layers showed n-type conduction. Free carrier concentration determined by Hall-effect and optical absorption in the near -infrared range (1-2 μm) was found to range between 2 and $6 \times 10^{17} \text{ cm}^{-3}$. Electron mobility varied from 30 to $80 \text{ cm}^2/\text{V s}$.

Preliminary we measured luminescence properties of these samples. First samples group had intensive light blue luminescence peaked at 2.5 - 2.7 eV defined probably by Mg or Zn impurity. The CL - spectra of these specimens were rather homogeneous. But the areas around the cracks emit a light shifted to yellow part of CL-spectrum (Fig.5.2.1).

Other samples grown in a more pure media show very weak violet or yellow emission depending on the growth conditions, structural and morphological quality of the epilayers. Some samples of this group have very low intensity of emission for visual interval of wavelengths. Typical low-temperature ($T=2 \text{ K}$) luminescence spectrum of such GaN sample is presented in the Fig. 5.2.2. This spectrum has strong, sharp bound exciton line at 3.47 eV .

In Fig.5.2.3 we can compare the room temperature photoluminescence of various initially undoped GaN samples. For the the most part of samples of this group the donor bound exciton recombination at 3.47 eV is more weak. But we see wide band yellow luminescence at 2.2 - 2.5 eV . Both bands of luminescence are observed also at low temperatures. The ratio of intensities of exciton to yellow bands depends highly on growth condition (growth temperature, inward flux of ammonia) and can be taken as a measure of the quality of the samples. In the best samples the intensity ratio was $30:1$ and the donor bound exciton had a line width of 4 meV .

Using SEM:CL method we found that the samples of initially undoped GaN epilayers demonstrates a spatial inhomogeneous luminescence in the energy interval $2.2 - 2.7 \text{ eV}$.

It was shown that typical luminescence inhomogeneities were recognized on the surface and in the cross section of epilayers. Under high magnification we measure in large quantities of separate bright green spots stand out sharply against the weak luminesced epilayer (Fig. 5.2. 4) We can also observe local bright yellow or blue spots and strips. Usually we observe areas with bright luminescence near morphological defects of the surface.

The cross section surface of GaN / SiC is demonstrated by Fig. 2.5 (substrate is located at the left-dark area). GaN-layer has a set of light stripes in parallel to the substrate with different luminescence spectra and intensity. As a rule the layer attached to the substrate surface emits in the blue which transforms to a yellow stripe with decrease of intensity. Part of

the GaN layers emitted very weak CL. Sometimes a blue needlelike formation crossed the GaN epilayer in the growth direction. As a result we are able to see the blue spots on surface.

Studies of GaN layers have shown that real space CL inhomogeneities can not be explained only taking into account the impurities as the epilayers are inhomogeneous, with different levels of impurities, different density of dislocations (across the bulk), and stoichiometry variations. We observed a distribution of defects for specimens grown at uniform impurity composition in external phase. We didn't measure an effect of crystallographic orientation dependence on the CL spectrum. However, the CL spectrum of shaped crystals didn't depend on orientation and changed during the growth process only. Therefore, we believe that the variation in CL spectra mainly depends on local stoichiometry deviation. The latter is a very complicated function of temperature, rate of ammonia flow, etc. One of possible reason of the yellow band existence in CL it is attributed to defects including Ga-vacancies [5,15]. Different impurity vacancy associations are responsible for different CL-bands [1]. Another factor which modifies the CL spectrum of GaN is a biaxial strain arising from substrate layer lattice mismatch [3].

5.2.4. Conclusion

Luminescence properties of GaN epilayers grown by sublimation sandwich-method on the SiC and sapphire substrates have been studied. The spatial inhomogeneity luminescence with different emission spectrum (from yellow to blue and violet) was observed in initially undoped epilayers both over the surface and cross-sections. It is noted the correlation between inhomogeneity of CL emission and morphological and structure defects of epilayers. It is suggested that local stoichiometric variations are responsible for inhomogeneity of luminescence. Interface layer between SiC-substrate and GaN- epitaxial layer with blue emission was discovered.

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5.3. Electron paramagnetic resonance of impurities. Identification of iron transition group trace impurities in GaN bulk crystals by electron paramagnetic resonance.

5.3.1 Introduction

GaN is considered to be one of the most promising semiconductor materials for the construction of short-wavelength emitting devices, such as blue diodes and lasers [1]. In spite of impressive technological achievements of the last few years, there are still substantial gaps in our knowledge of the basic physical properties of GaN. One of them concerns the identification of transition metal impurities in GaN. The presence of these impurities in semiconductors influences the materials' characteristics and device performance. An important question concerns the future of transition-metal impurities as compensators in order to obtain semi-insulating substrates.

The EPR proved to be a powerful method for the identification of transition metal impurities in semiconductors. By now only Fe^{3+} ions were investigated in GaN using EPR [2,3]. The sublimation sandwich-method was used for growing GaN crystals as thick as 0.1 mm [4,5]. It was reported [6,7], that these crystals have good characteristics, no worse than in thin GaN layers grown by other techniques. These crystals have shown at least three zero-phonon lines of photoluminescence in infrared spectrum range: 1.3 eV, 1.19 eV, 1.047 eV [6,7]. It was supposed, that these lines belong to transitions within 3d levels of trace impurities of transition metal ions. The investigations of optically detected magnetic resonance have shown the correspondence between the EPR spectra, attributed to Fe^{3+} , and 1.3 eV luminescence line. The nature of other lines was widely discussed. The experimental results on the 1.047 eV emission [8] fit to a ${}^4\text{T}_2(\text{F})\text{-}{}^4\text{A}_2(\text{F})$ internal electronic transition of a transition metal with a $3d^7$ electronic configuration. It was suggested [9] that the best candidate was Co^{2+} , but the author could not completely exclude the Ni^{3+} . Thus, only correlation with the EPR seems can clarify this problem. It should be noted that the emission at 1.047 eV has not been observed as natural contaminant in GaN samples grown by metal organic vapor phase epitaxy and vapor phase epitaxy.

5.3.2. Experimental and discussion

We report here new EPR results for Mn^{2+} and Ni^{3+} in GaN grown by the sublimation sandwich method. Preliminary reports on Mn^{2+} in GaN have been published elsewhere [9].

In this work we investigated GaN crystals grown on 6H-SiC substrates by the sublimation sandwich method [4,5]. The thickness of GaN epitaxial layers was 0.1-0.2 mm and we can say with reasonable confidence that GaN was a bulk material in our experiments. Epitaxial layers on substrates and free-standing layers were used. No intentional doping of samples was performed. The samples were oriented for rotation in the $\{11\bar{2}0\}$ plane. The EPR spectra were studied on a conventional X-band (9.25 GHz) EPR spectrometer in the temperature range 4 - 150 K.

Fig. 5. 3.1 shows a part of the EPR spectrum of a GaN epitaxial layer on a 6H-SiC substrate, recorded at $T=4$ K for several angles (θ) between the applied magnetic field and the hexagonal axis (c -axis) of the sample (rotation in the $\{11\bar{2}0\}$ plane). In Fig. 3.1 a set of six equally intense lines can be seen on both sides of the central line. The strong signal near 3300 G contains, except the central fine-structure line of Fe^{3+} , a signal from the nitrogen donor impurity in the 6H-SiC substrate. The latter was nearly suppressed upon removing the substrate. In the orientations $B \parallel c$ and $B \perp c$ these lines are marked by a set of vertical lines. The separations between the lines are about 70 G. We could observe other four groups with smaller intensities on both sides of central one, which proves that this spectrum belongs to an ion with electron spin $S=5/2$. All the groups have the same hf structure as the central one. Among the transition metal elements only manganese has a 100% abundant isotope with nuclear spin $I=5/2$ and the observed splitting corresponds to that of Mn^{2+} in $3d^5$ ($^6S_{5/2}$) state. The group in Fig. 1 belongs to the Mn^{2+} central fine structure transition ($M_S = 1/2 \leftrightarrow M_S = -1/2$), split by the hf interaction with nuclear spin $I=5/2$.

An investigation of the angular dependence of the spectrum of Mn^{2+} allowed us to find the best-fit parameters for spin Hamiltonian. The results are listed in Table 1 (the small parameters $a-F \approx 4 \cdot 10^{-4} \text{ cm}^{-1}$ and $a \approx 5 \cdot 10^{-4} \text{ cm}^{-1}$ are not pointed out in the table). The measured and calculated angular dependencies of fine-structure line positions of Mn^{2+} ions obtained at 9.25 GHz are plotted as open circles and dashed lines, respectively, in Fig. 3.2. The fine-structure positions have been estimated as the center of gravity of the measured hf structure transitions. The solid circles and solid lines represent the measured and calculated hf structure positions, which are plotted only for central transition ($M_S = 1/2 \leftrightarrow M_S = -1/2$).

In Fig. 5.3. 1 for the orientations $\theta = 10^\circ$ and 15° one can see intense broad EPR line, attributed [2] to one of the fine-structure transitions of Fe^{3+} with electron spin $S=5/2$. With increasing temperature EPR signals of Mn^{2+} and Fe^{3+} decrease in a similar manner. Fe^{3+} and Mn^{2+} EPR signals are detectable up to ~ 100 K.

An intense anisotropic EPR line was observed in some GaN crystals. Fig. 3.3 shows an angular dependence of these line in GaN crystal at the X-band. The magnetic field applied was rotated in the $\{11\bar{2}0\}$ plane. This EPR spectrum has the characteristic anisotropy of an $S=3/2$ system in a strong axial crystalline field and positive g shift which is consistent with the electron configuration d^7 . The EPR line can be observed up to ~ 150 K and the linewidth is very sensitive to the orientation of the crystal in magnetic field. The intensities of the EPR signals for $\theta \neq 0$ at 77 K are lower and depend more on the angle between magnetic field and

c-axis then those at 4 K. Therefore it has not been possible to detect the signals at all angles at 77 K.

We attribute this spectrum to the trace impurity of nickel in the charge state Ni^{3+} . Isolated substitutional Ni^{3+} ion has a $3d^7$ electronic configuration.

In Ref.[2], an analogy was revealed between the parameters of Fe^{3+} ions in GaN and ZnO crystals. It was taken into account that both materials have the same hexagonal wurzite structure and close by similar physical parameters. We will follow this analogy in the case of Mn^{2+} and Ni^{3+} and the Table 1 lists corresponding values previously obtained for ZnO: Mn^{2+} [13] and ZnO: Ni^{3+} [12] (the parameters for Mn^{2+} in ZnO, $a-F=5.2 \cdot 10^{-4} \text{cm}^{-1}$ and $a=6.2 \cdot 10^{-4} \text{cm}^{-1}$, are not pointed out in the Table 1). As illustrated in Table 1, a good correspondence is observed between the parameters of Fe^{3+} , Mn^{2+} and Ni^{3+} in GaN and ZnO. The small quantitative variation in the EPR parameters seems to reflect the changing degree of covalence. By analogy with Fe^{3+} in GaN we suppose that manganese and nickel occupy gallium sites in the GaN lattice. Since no hf structure for the line which we attributed to Ni^{3+} was observed we could not completely exclude some impurities which are isoelectronic to Ni^{3+} and have small concentration of odd isotopes or a very small value of nuclear magnetic moment, e.g., Fe^+ or ions with $4d^7$ and $5d^7$ configurations.

According to our investigations we have every reason to think, that zero-phonon luminescence line at 1.047 eV belongs to transition ${}^4\text{T}_2(\text{F})\text{-}{}^4\text{A}_2(\text{F})$ within 3d levels of Ni^{3+} ion with a $3d^7$ electronic configuration. This luminescence line has been observed only in GaN samples grown by the sandwich technique and seems to correlate with EPR spectra of Ni^{3+} . This assumption is consistent with the experiments of Ref. [8] in which photoluminescence results on the 1.047 eV emission fit to a ${}^4\text{T}_2(\text{F})\text{-}{}^4\text{A}_2(\text{F})$ internal electronic transition of a transition metal with a $3d^7$ electronic configuration. It should be noted that Fe^{3+} (the same charge state as Ni^{3+}) has the stable configuration in *n*-type GaN material and it's EPR spectra have been observed in the same samples in which the EPR spectra of Ni^{3+} were recorded.

On the basis of the EPR investigations we have estimated the impurity concentrations in several GaN crystals used in our experiments at $10^{17} - 10^{18} \text{cm}^{-3}$ for Fe, and $10^{16} - 10^{17} \text{cm}^{-3}$ for Mn and Ni. We would finally like to comment on possible sources of Fe, Mn and Ni contaminations in GaN crystals grown by the sandwich sublimation technique. Fe and Mn contamination during the growth process may result from container material of the Ga source. Ni contamination may result from SiC substrate which was etched in molten KOH with using of the container from the nickel material.

In addition, the energy level scheme of transition metals in GaN, as inferred from known levels in other III-V compounds via the Langer Heinrich rule, indicates, that the acceptor levels of Mn and Ni are close to mid-gap [14]. Therefore Mn and Ni seem to be more suitable dopants for the creation of semi-insulating GaN substrates as previously discussed Fe and Cr.

In some GaN samples the EPR spectra of shallow donors were detected. Fig. 5.3.4 shows the EPR spectra of shallow donors (single line at 3400 G). The strong line at 3300 G is due to the nitrogen donors in 6H-SiC-substrate. The *g*-factors for this line are: $g_{||} = 1.9547$, $g_{\perp} = 1.9520$, which coincide with those reported earlier [15]

5.3.3. Conclusion

We report on the observation of electron paramagnetic resonance of iron, manganese and nickel trace impurities in bulk GaN crystals grown by the sublimation sandwich method. The resolved hyperfine structure due to interaction with ^{55}Mn ($I=5/2$) nuclei has been observed in GaN, allowing unambiguous identification of the impurity. Manganese and nickel exist in Mn^{2+} ($3d^5$) and Ni^{3+} ($3d^7$) charge states with electron spin $S=5/2$ and $S=3/2$, respectively, and occupy gallium sites in the GaN lattice. For Mn^{2+} we found $g=1.999$, hyperfine structure constant $A=70\cdot 10^{-4}\text{cm}^{-1}$ and fine structure parameter $|D| = 240\cdot 10^{-4}\text{cm}^{-1}$. The EPR spectrum of Ni^{3+} in GaN had the characteristic anisotropy of an $S = 3/2$ system in a strong axial crystalline field. The effective g -factor values were found to be $g_{||}' = 2.10$ and $g_{\perp}' \cong 4.20$ for a system with an effective spin $S' = 1/2$. An analogy was revealed between the parameters of Mn^{2+} and Ni^{3+} in GaN and ZnO crystals. The zero-phonon line at 1.047 eV seems to belong to transition ${}^4\text{T}_2(\text{F})\text{-}{}^4\text{A}_2(\text{F})$ within 3d levels of Ni^{3+} ion with a $3d^7$ electronic configuration.

5.3.4. Selected bibliography

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6. SUMMARY

The basic investigations leading to the fabrication of thick (more than 0.2 mm) monocrystalline layers of GaN on the silicon carbide substrates. GaN layers were grown by sublimation sandwich-method in ammonia atmosphere. GaN polycrystalline powder and metallic Ga were used as a vapor source. The growth was carried out in quartz reactors both horizontal, and vertical types, in furnaces with high-frequency heating.

The analysis of the substrates for thick layers GaN growth with use of being available literary data are presented. Results of the analysis let us to choose a substrate from hexagonal SiC (α -SiC). Main advantages these substrates are their inertness to conditions of layers GaN growth, affinity presence both the lattice parameters ($\Delta a/a=3.4\%$) and thermal expansion coefficient (distinction in LEC=33%). We offer the ways of reduction of that discrepancy with using Al-doped substrates, previously radiated by high-energy particles.

The possibility of growing of thick monocrystalline GaN layers at growth temperature range from 1200 to 1230⁰C without preliminary deposition of buffer layers with very high speeds up to 1 mm/h is shown.

Rocking curve measurements of the GaN layers grown by SSM reveal the full width of half maximum (FWHM) from 150 to 400 arc.sec. Three-dimensional 15-20 arc.sec. disoriented wurtzite domains looked like the hexagonal prisms in size of cells of 50 nm were found. Correlation between the spectral luminescence characteristics, its spatial inhomogeneity and structural perfection of the grown layers was shown. Increasing of wide-band emission in visual spectrum and its spatial inhomogeneity was suggested to be caused by the local stoichiometry deviation. The Fe, Ni, Mn impurities states in the GaN crystals were discovered and identified by the EPR method.

The further improvement in crystal quality of GaN thick layers requires elimination of the following constructive lacks of the growing system, namely the ensuring stabilization of the operating modes of high-frequency heater and automation of temperature control in the growth cell. It is desirable to use the SiC substrates having previously deposited buffer layer of monocrystalline GaN .

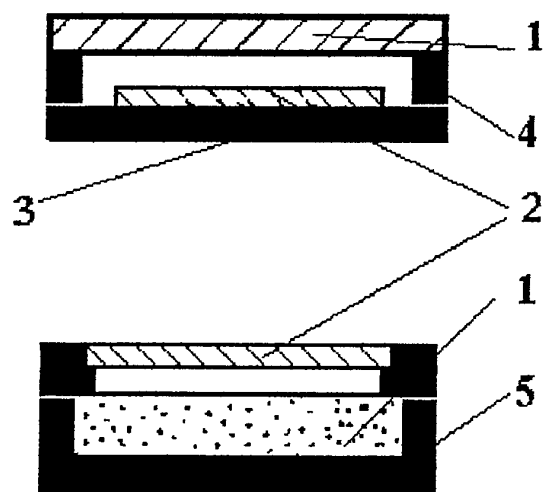


Fig.1.1. Two types of sandwich cells

1- source; 2 - substrate ; 3 - plate;
4-ring; 5 - cup

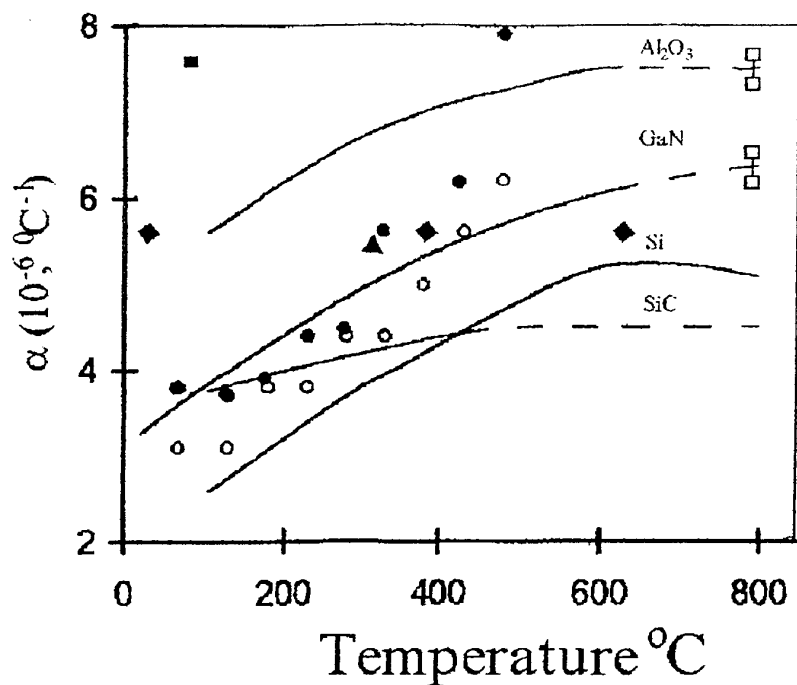


Fig.2.1. Dependence of thermal expansion coefficients of SiC, Si, GaN and Al_2O_3 on temperature

Data of Si, SiC and Al_2O_3 from book: Fizicheskie velichini. Ed. by E.M.Voronkova et al, Moskow, 1991

Experimental points for GaN from [16] and [19] and our evaluations.

Table 2.1

Properties of prospective nitride substrates.

Substrate material	Symmetry	Lattice parameters Å	Coefficient of thermal expansion $\times 10^{-6}/K$
GaN-WZ	Hexagonal	a=3.189 c=5.185	5.59
GaN-ZB	Cubic	a=4.503	3.17
AlN	Hexagonal	a=3.112 c=4.9825	4.2 5.3
6H SiC	Hexagonal	a=3.08 c=15.12	4.2 4.68
Sapphire	Hexagonal	a=4.758 c=12.99	7.5 8.5
ZnO	Hexagonal	a=3.252 c=5.213	2.9 4.75
LiAlO ₂	Hexagonal		5.4
GaAs	cubic	a=5.6533	6.0
3C-SiC	cubic	a=4.36	
MgO	cubic	a=4.216	10.5
InP	cubic	a=5.8693	4.5
GaP	cubic	a=5.4512	4.65
MgAl ₂ O ₄	cubic	a=8.083	7.45
Si	cubic		2.5

The data from Landolt - Bornstein (Springer, New York, 1982), V.17

Table 2.2

Substrate Materials for GaN

Material	Structure	% Mismatch, ($\Delta a/a$)
AlN	Wurtsite	2.4
Sapphire	Wurtsite	8.3; 13.8*; 16**
GaAs	Zinc blende	9.0
GaP	Zinc blende	5.2
Si	Cubic	4.8
6HSiC	Hexagonal	3.4
3C SiC	Zinc blende	3.15
SiO ₂		4.05
LiAlO ₂	Wurtsite	1.45**
ZnO	Wurtsite	0.2

The data from [3, ch.1]; *- from [14]; ** - from[3]

Table 3. 1

X-ray diffraction study of SiC substrates grown by different methods:

Lely - free-standing Lely crystals

SSM - bulk crystals grown by crystals grown by sublimation sandwich - method

№	Method of growth	Polytype	Rocking curve	FWHM
1	Lely	6H	0006	13"
2	Lely	6H	0006	24"
3	Lely	6H	0006	15"
4	Lely	6H	0006	15"
5	SSM	6H	0006	17"
6	SSM	6H	0006	24''
7	SSM	6H	0006	22''
8	SSM	4H	0006	24"
9	SSM	4H	0006	15''
10	SSM	4H	0006	16"

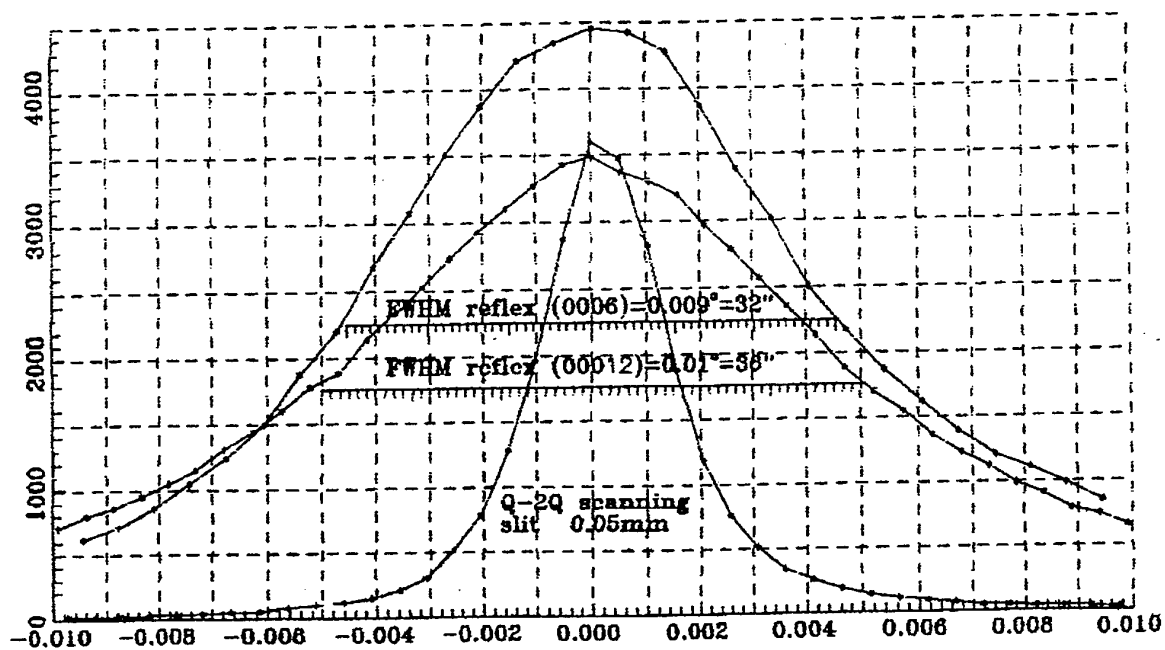


Fig. 3.1. Usual rocking curve for SiC Lely substrate. Sample 603 Monochromator Lely (0006).
 $W_{(0006)} = 17.75^\circ$, $W_{(00012)} = 37.50^\circ$.

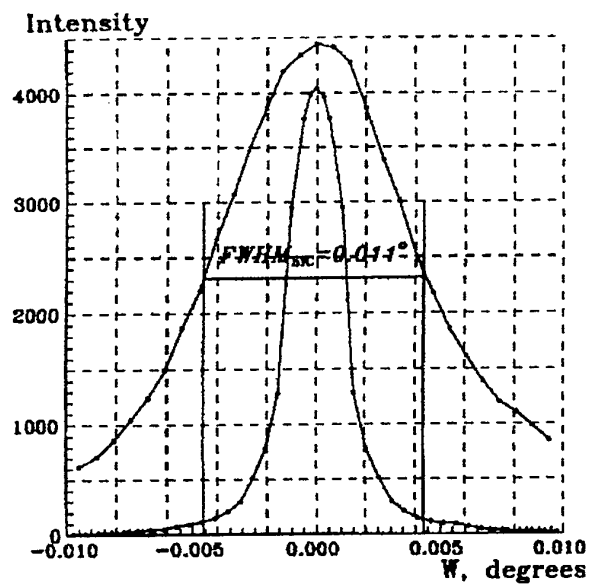


Fig. 3.2. W-scanning of SiC substrate defect place
 reflex (0006), $W_0 = 17.85^\circ$
 $FWHM = 0.011^\circ (=40 \text{ arc. sec})$
 The same for polished and etched place
 $FWHM = 0.0038^\circ = 14''$

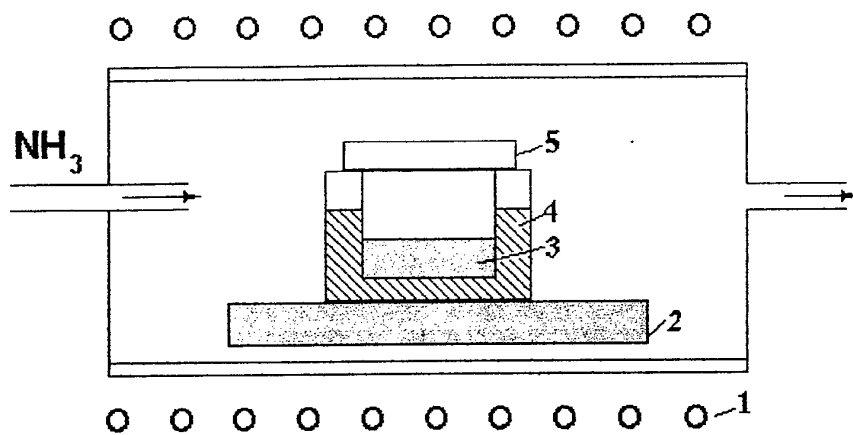


Fig.4.1 Experimental setup for growth of GaN layers by SSM

1 - Inductor 2 - Susceptor 3 - Vapor source 4 - Container
5 - SiC substrate

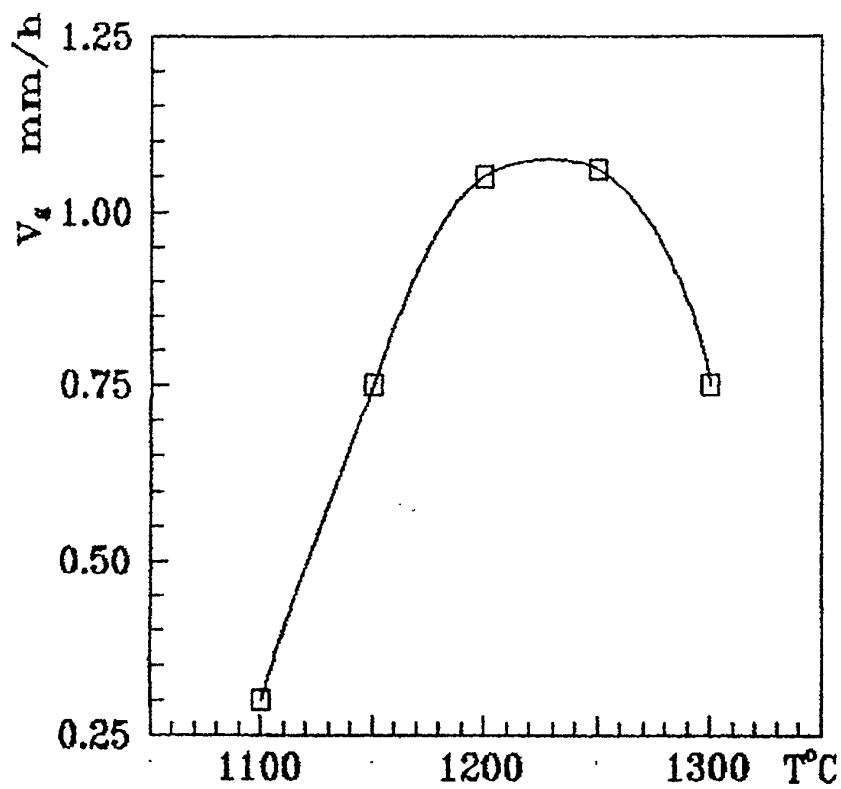


Fig. 4.2. Dependence of GaN layers growth rate on temperature

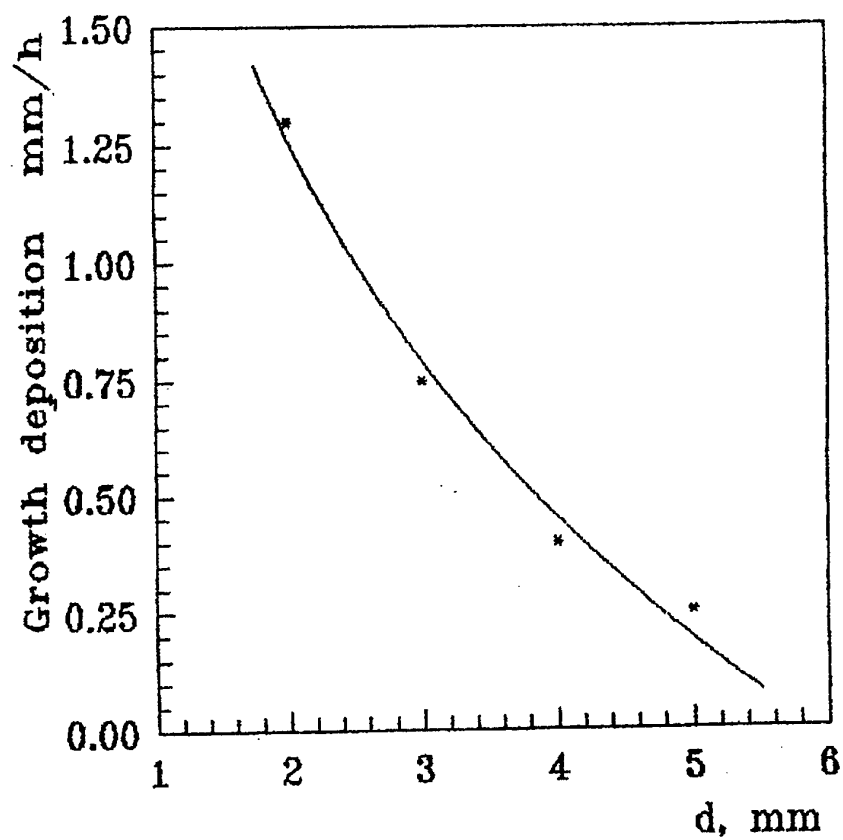


Fig. 4.3. Dependence of GaN layers growth rate on clearance between substrate and source

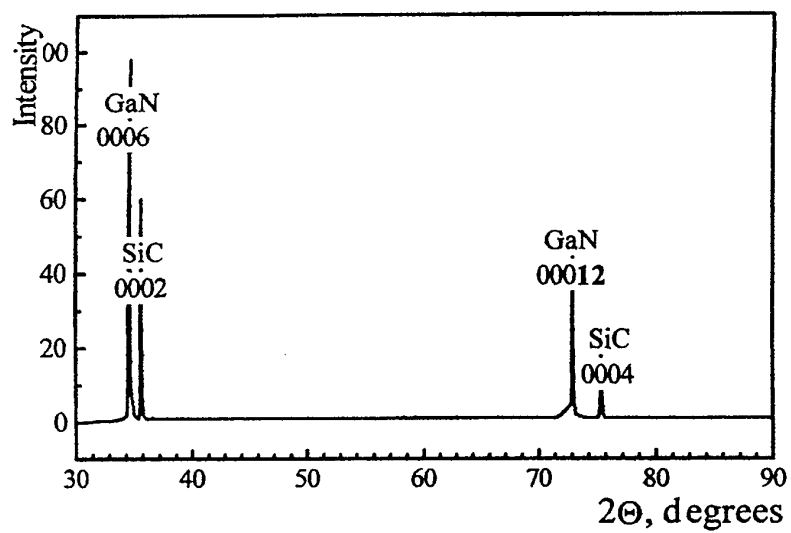


Fig 5.1.1.1. X-ray diffraction pattern for GaN layers deposited on 6H-SiC (0001) substrate by SSM. (0002) & (0004) peaks from SiC and (0006) & (00012) from GaN observed in Θ - 2Θ scan.

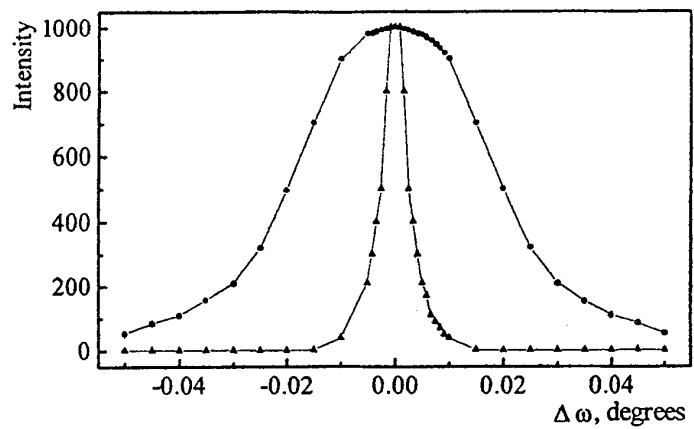


Fig. 5.1.2. Comparison the shape of XRD
 \otimes - (0002) SiC substrate and for
 ∇ - (0006) GaN epilayer by ω -scan.

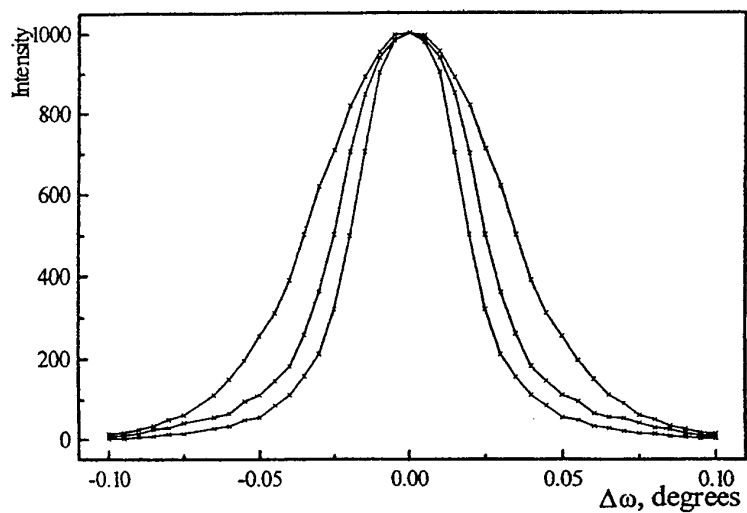


Fig. 5.1.3. Typical rocking curve from different heterostructures GaN/SiC.

- a). GaN/SiC No 1364. FWHM = 150''
- b). GaN/SiC No 1520 FWHM = 180''
- c). GaN/SiC No 1645 FWHM = 350''

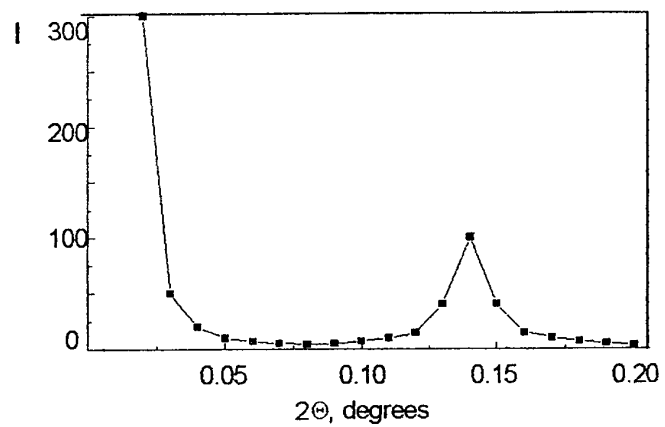


Fig.5.1.4 . X-ray diffraction profiles for S AS of GaN film deposited on SiC substrate. It is seen the peak near 0.135° - 0.15° This value corresponds (using Wulf-Bragg dependence: $2d\sin \Theta = n\lambda$) 65nm-50nm

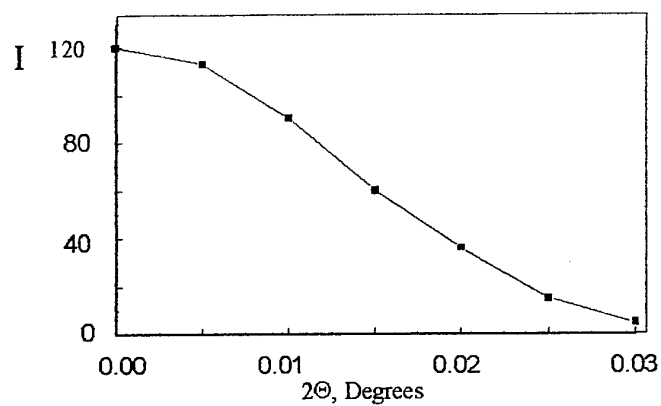


Fig. 5.1.5. Dependence intensity of S AS versus angle for GaN film deposited on Al_2O_3 substrate. Smooth curve of broadening incident beam. This corresponds to gas-like allocation of domains.

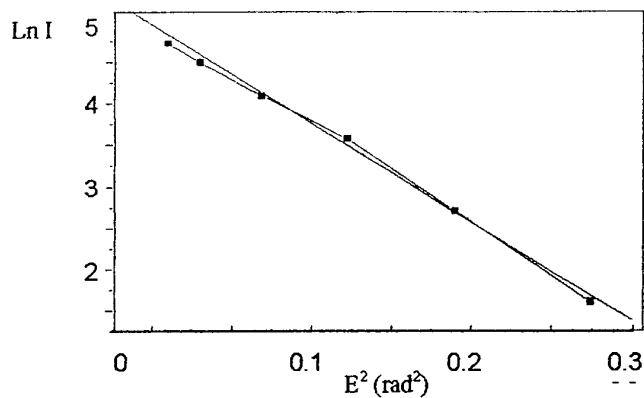


Fig.5.1.6 . Logarithmic dependence intensity of S AS versus scattering square angle for GaN film deposited on Al₂O₃ substrate. Linear approximation of this dependence shows coefficient for measurement of distances between clusters in GaN film. In this case $Y=B \cdot X + X_0$; $B=1.17E007$ Distance $R_0=0.644 \cdot \sqrt{B}=220\text{nm}$ in this case.



Fig.5.2.1. Real CCL+BSE-SEM image of the surface of the GaN epilayers grown on SiC-substrates.
Effective blue luminescence and yellow stripes around cracks.

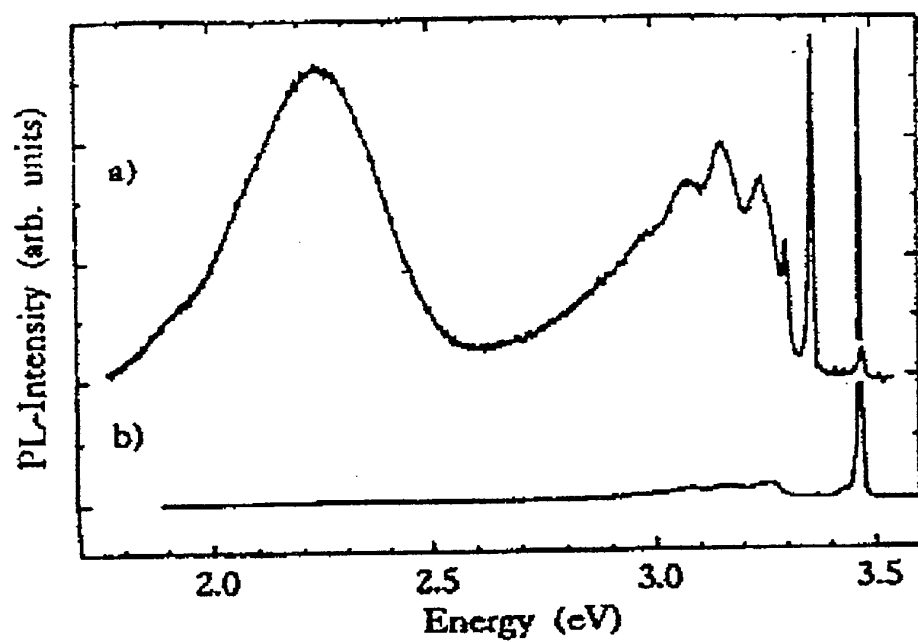


Fig. 5.2.2. Photoluminescence spectra in the near ultraviolet and visible spectral range of two samples GaN on 6H-SiC under 325 HeCd laser excitation ($T=2$ K)

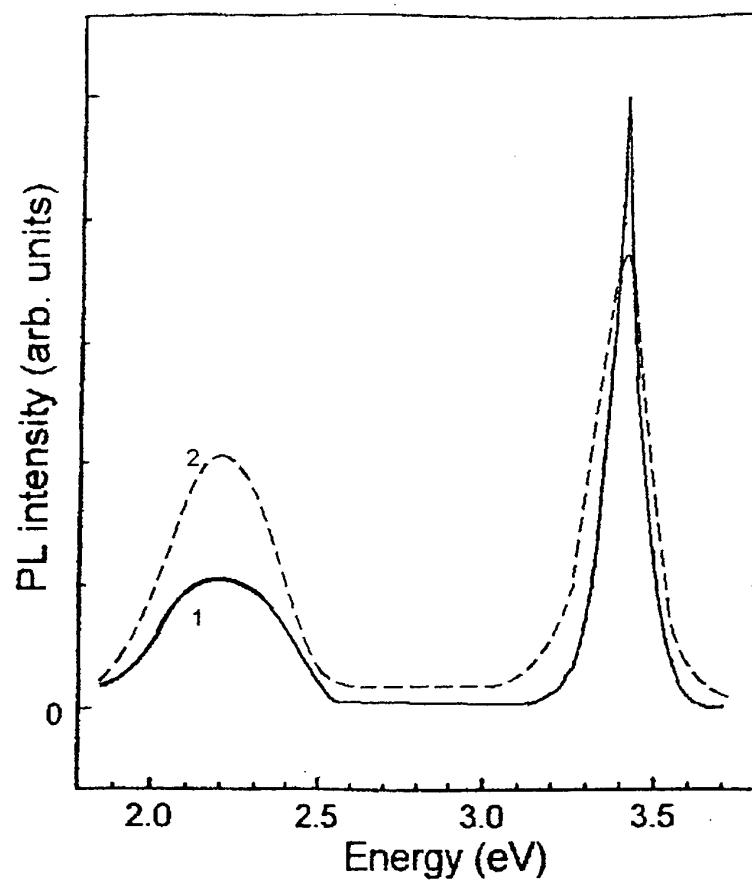


Fig. 5.2. 3 Photoluminescence spectra at room temperature for two GaN epilayers grown on SiC substrates at different temperatures $^{\circ}\text{C}$; 1140 - solid curve; 1210 - dotted curve.

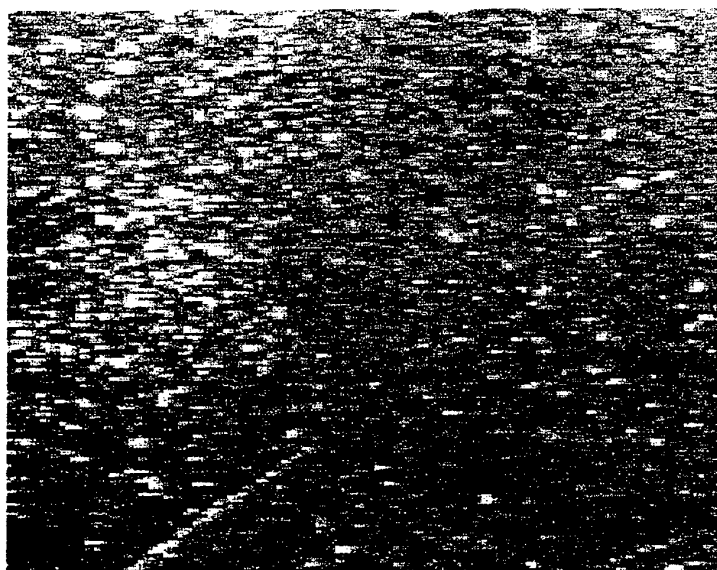


Fig.5.2.4. Real CCL-SEM image of the surface of the initial undoped GaN epilayers grown on SiC substrate. Separate bright greenish spots are seen.

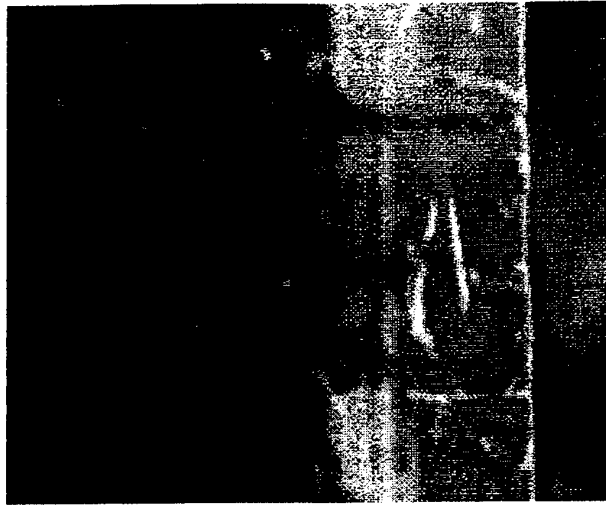


Fig.5.2.5Real CCL - SEM image of cross-section of the GaN epilayer grown on SiC substrates (0.3 mm thickness). Blue stripe is interface layer between substrate (at the left) and grown GaN-epilayers (at the right).

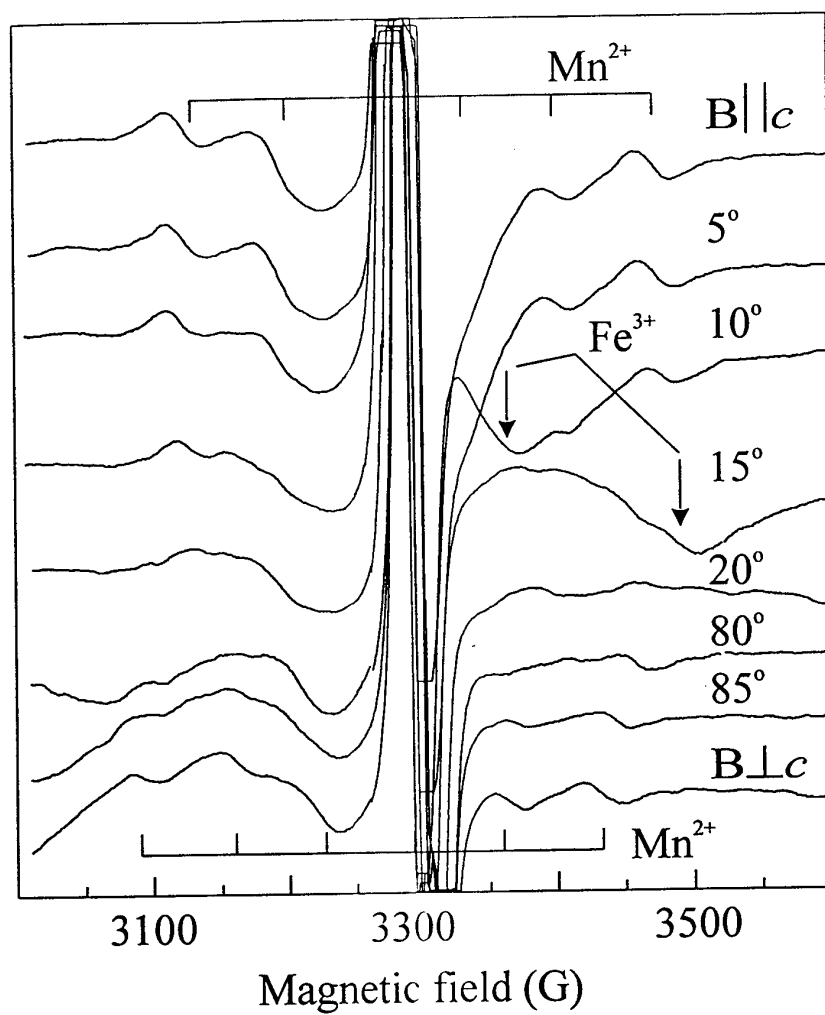


Fig. 5.3.1. EPR spectrum of Mn²⁺ ions in GaN in some orientations of crystal under rotation in {11 $\bar{2}$ 0} plane. In orientations B//c and B⊥c the positions of hf structure transition of Mn²⁺ ($M_s=1/2$ $M_s=-1/2$) are indicated. The arrows indicate positions of Fe³⁺ EPR signal.

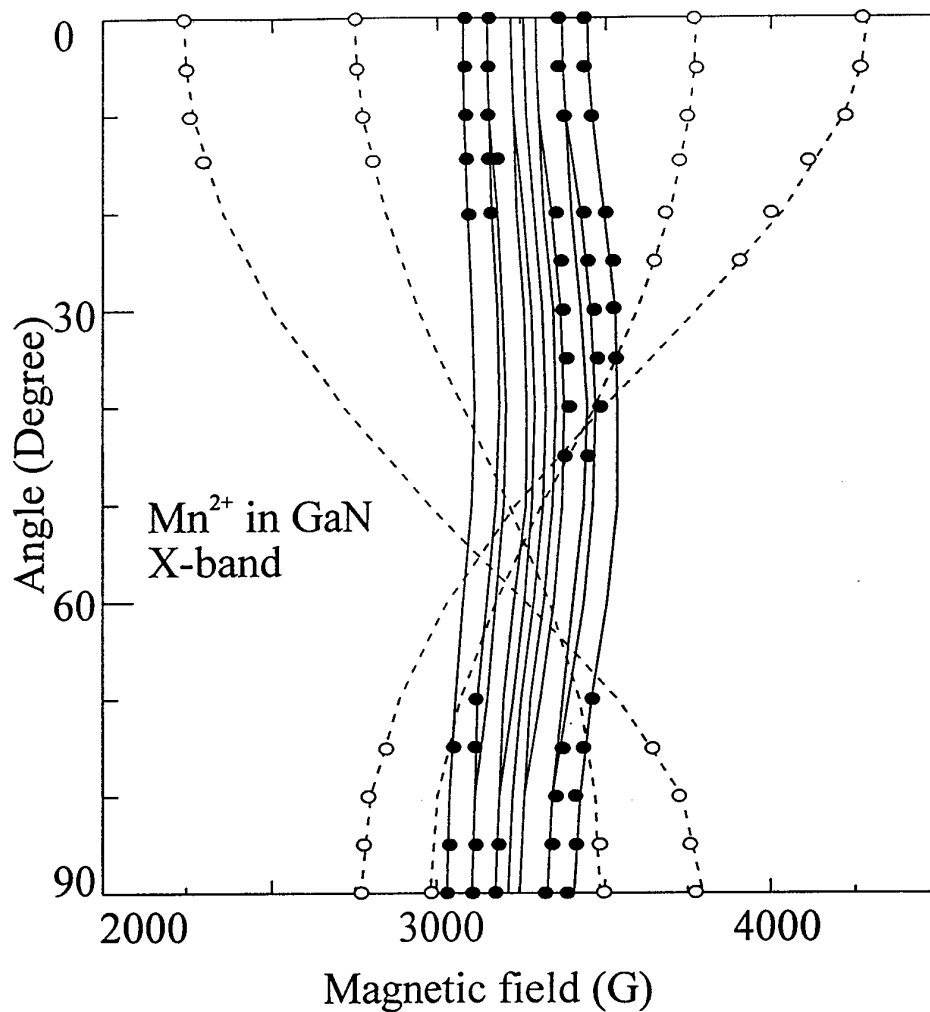


Fig. 5.3.2. The measured (open circles) and calculated (dashed lines) angular dependencies of fine-structure line positions of Mn²⁺ ions in GaN obtained at 9.25 GHz. The solid circles and solid lines represent the measured and calculated hf structure positions, respectively, which are plotted only for central transition ($M_s = 1/2$ $M_s = -1/2$).

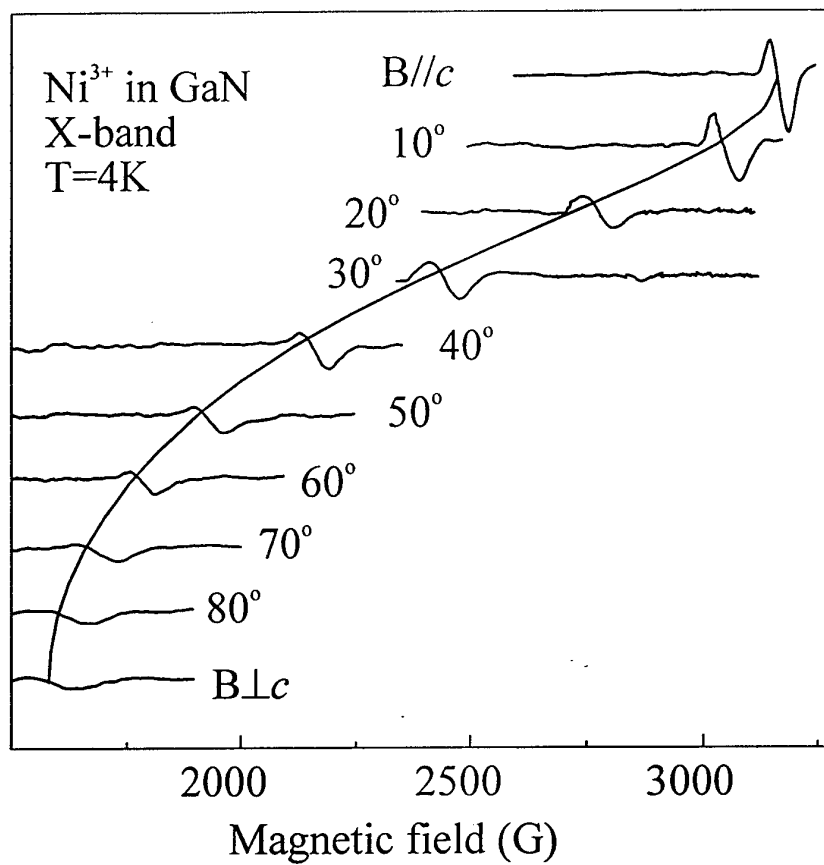


Fig. 5.3.3. Angular dependence of Ni^{3+} EPR line for rotation of the GaN crystal in $\{11\bar{2}0\}$ plane. Solid line have been calculated using spin Hamiltonian parameters of Eq. (2), listed in the table.

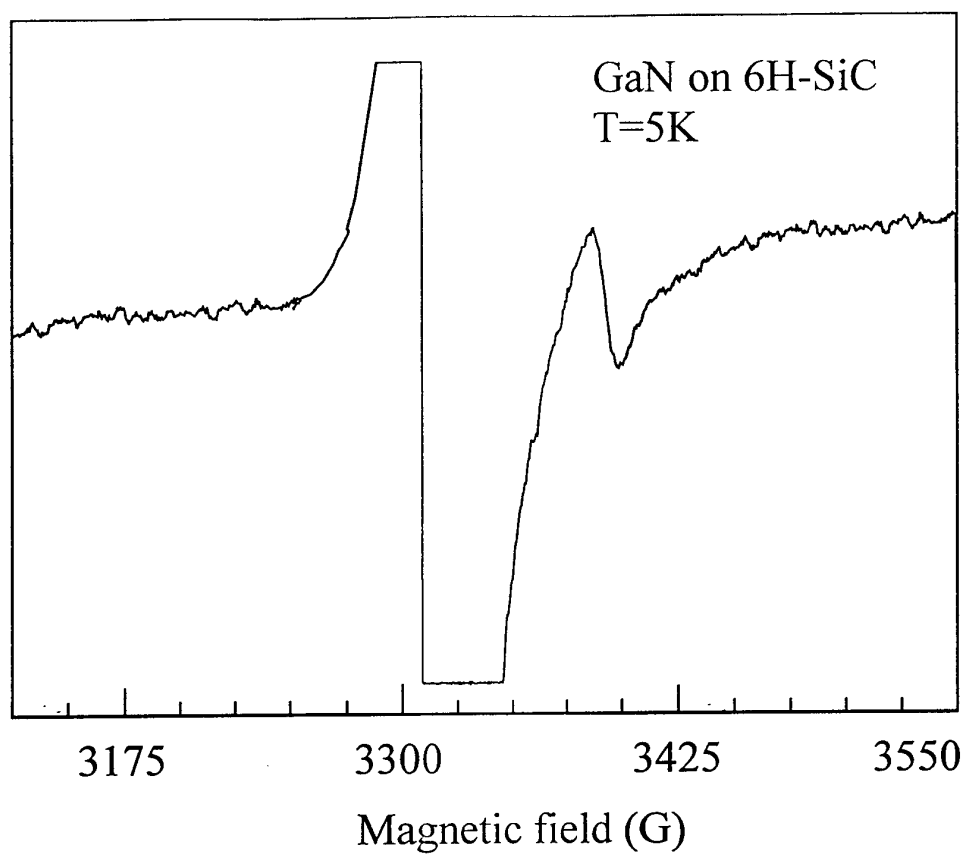


Fig. 5.2.4. The EPR spectrum of shallow donors in GaN in orientation $B//c$. The strong central line belongs to nitrogen donors in 6H-SiC substrate.

Table 5.1. The parameters of the spin Hamiltonian of Eq. (1) for Fe^{3+} and Mn^{2+} ions
and of the spin Hamiltonian of Eq. (2,3) for Ni^{3+} ions in GaN and ZnO.

	GaN					ZnO				
	g_{\parallel}	g_{\perp}	$D/10^{-4}\text{cm}^{-1}$	$A/10^{-4}\text{cm}^{-1}$	Ref.	g_{\parallel}	g_{\perp}	$D/10^{-4}\text{cm}^{-1}$	$A/10^{-4}\text{cm}^{-1}$	Ref.
Fe^{3+} ($3d^5$)	1.990 1.995	1.997 1.995	713 715		[2] this work	2.006	2.006	-595		[2]
Mn^{2+} ($3d^5$)	1.999	1.999	240	70	this work	2.001	2.001	-236	74.1	[13]
Ni^{3+} ($3d^7$)	2.10 2.10	$\cong 4.2$ $\cong 2.1$	$\geq 1.5 \cdot 10^4$		this work $S'=1/2$ $S=3/2$	2.142 2.142	44.318 $\cong 2.16$	$+2 \cdot 10^4$		[12] $S'=1/2$ $S=3/2$